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PACKAGING

V. THE GREASE RESISTANCE OF SOME COMMON PACKAGING MATERIALS[1]

By C. G. Lavers[2]

Abstract

The grease resistance of a wide variety of packaging materials was tested before and after creasing and ageing, using a modification of TAPPI method T454 *m*-44. Kraft and sulphite were of little or no value as grease barriers even after paraffin wax coating or impregnating. Vegetable parchment and 'greaseproof' paper were superior to kraft. The grease resistance of glassine was 5 to 10 times greater than that of either greaseproof paper or vegetable parchment. Polyethylene, in turn, was considerably more resistant than glassine, and just slightly less resistant than all grades of "Cellophane", and cellulose acetate, cellulose nitrate, ethyl cellulose, Pliofilm, vinylite, and Saran.

Creasing glassine caused large reductions in its grease resistance, especially when heavy basis weights were tested. Paraffin wax coatings seemed to be more effective in improving grease resistance when dense base stocks were used. On kraft, a heavy wax coating was necessary to produce a small improvement, while on glassine only a very light coating was required, to bring about considerable improvement in grease resistance. Ageing many materials at 140° F. markedly reduced their grease resistance. An exception to this was glassine, most samples of which had greater resistance to grease penetration after ageing. Neither ageing nor creasing appreciably affected the grease resistance of Cellophane, or the thermoplastic films tested.

Introduction

To design a suitable package for a particular food, a knowledge of the mechanical strength, water-vapour resistance, sealing properties, grease resistance, etc., of many packaging materials is usually necessary. Earlier publications in this series have dealt with the water-vapour transmission and mechanical strength of several packaging materials (2, 3). The purpose of the present study is to evaluate the grease resistance of many of the materials commonly used in food packaging.

Materials and Methods

The materials tested included kraft, sulphite, cellucine, glassine, vegetable parchment, manilla, 'greaseproof' paper, "Cellophane", and several thermoplastic films including cellulose acetate, cellulose nitrate, ethyl cellulose, vinylite, polyethylene, Saran, and Pliofilm. Many of the materials were

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examined in both the waxed and unwaxed states and at several different basis weights. A detailed description of all samples studied is given in Table I.

The method of testing grease resistance was essentially that described in TAPPI method T454 *m*-44, with certain modifications. By this method a small pile (5 gm.) of sand is placed on the sample to be tested, to this is added 1.1 ml. of turpentine containing a red dye, and the time required for the coloured turpentine to penetrate the sample and stain a sheet of white paper placed beneath it is measured. The samples were not conditioned and tested at a fixed temperature and humidity as required by T454 *m*-44, all determinations being done at room conditions (approximately 75° F., 35% relative humidity). The TAPPI standard test for grease resistance also states that 30 specimens of each sample should be tested. In this study 15 specimens of unaged, and five of aged, samples were tested. This reduction in the number of specimens tested was believed to be justified because preliminary trials had shown that variations between samples of one type of material from different sources were greater than the variations between different specimens of a single sample. Since samples were available from a single source only and were often taken from the same roll, it was considered that the number of determinations done gave sufficiently accurate values for a particular sample, and for setting up a relative scale for comparing the various materials.

The relative scale used was as follows:

Time for dye to penetrate sample, sec.	Grease resistance score
0 - 50	0
50 - 500	1
500 - 1000	2
1000 - 2000	3
2000 - 4000	4
4000 - 8000	5
8000 - 18000	6
>18000	7

The large number of determinations that had to be done necessitated the adoption of a more convenient procedure than moving each sample to see if penetration had occurred. To overcome this difficulty, a low platform (18 in. high) with a glass top was placed on the laboratory bench. This was illuminated from below with a fluorescent light of suitable length. Samples were then placed on the top of the glass sheet, replacing the white book paper of T454 *m*-44 with a thin tissue that the coloured turpentine penetrated instantly. With this arrangement test specimens could easily be examined for penetration from underneath without moving any samples, making it possible to do many determinations simultaneously.

Since the grease resistance of a creased sheet may be considerably less than that of the uncreased material, samples were tested both before and after creasing. The method of creasing has been described.* Briefly it consists in making two creases in the material crossing at right-angles by folding first in one direction and then in the opposite, the crease being produced by placing a 1 lb. weight on the loosely folded material.

To simulate long term storage under dry conditions samples were aged for one week at 140° F., low humidity (approximately 6%), conditioned for 24 hr. at room temperature and humidity, and their grease resistance subsequently tested.

Results

Grease resistance scores are given in Table I. Values that are recorded as 7 indicate that penetration did not occur in five hours. Tests were not run longer than this because it was found that at the end of five hours almost all the turpentine had evaporated.

When untreated (i.e., unwaxed, not laminated, and not aged or creased) base stocks were considered, it was obvious that kraft and ordinary sulphite papers were of little or no value as grease barriers. Vegetable parchment and 'greaseproof' paper had approximately equal resistances, and were superior to kraft. Although the values obtained for greaseproof paper were rather low, materials of this type can be produced with very high grease resistance, as shown by the commercial sheets designated in Table I as Lard Liners and Shortening Papers. The very high resistance of these materials was probably a result of the type of pulp used, and the treatment applied to it in the beater (1). The grease resistance of most samples of glassine was 5 to 10 times greater than that of either greaseproof paper or vegetable parchment. Polyethylene was considerably more resistant than most samples of glassine, but less resistant than Cellophane, cellulose acetate, cellulose nitrate, ethyl cellulose, Pliofilm, vinylite, and Saran.

Creasing unwaxed and unaged samples of many materials caused considerable reduction in their grease resistance. This was especially noted with glassine. For this material, the reduction in grease resistance score upon creasing became greater as the basis weight of the sample increased. Creasing did not appreciably affect the grease resistance of Cellophane or the various thermoplastic materials tested.

The effectiveness of paraffin wax in improving grease resistance appeared to depend largely on the nature of the base sheet to which it was applied. On kraft, dry waxing, i.e., wax impregnating, had little beneficial effect. Kraft, paraffin coated on one side, did not show any improvement in grease resistance until a basis weight of 60 lb. per ream (ream weights refer to 500 sheets, 24 by 36 in.) was used with a 12 lb. wax coat. Samples coated on both sides showed some resistance when 25 lb. material was waxed to 35 lb.

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* *Wrapping greaseproof. Canadian Packaging Committee Code 105. Sept. 15, 1945. Currently available from Forest Products Laboratories, Department of Mines and Resources, Ottawa, Canada.*

TABLE I

THE GREASE RESISTANCE OF SOME COMMON PACKAGING MATERIALS

Material		Grease resistance score			
		Materials as received (average 15 determinations)		Materials aged one week at 140° F. (average 5 determinations)	
		Flat	Creased	Flat	Creased
Kraft					
50 lb.		0	0	0	0
30 lb. dry waxed to 36 lb.		0	0	0	0
45 lb. dry waxed to 55 lb.		0	0	0	0
15 lb. waxed one side to 20 lb.	Wax up	0	0	0	0
	Wax down	0	0	0	0
28 lb. white, waxed one side to 31 lb.	Wax up	0	0	0	0
	Wax down	0	0	0	0
30 lb. waxed one side to 38 lb.	Wax up	0	0	0	0
	Wax down	0	0	0	0
60 lb. blue, waxed one side to 72 lb.	Wax up	1	0	1	0
	Wax down	3	0	1	0
25 lb. waxed two sides to 35 lb.		2	0	1	0
25 lb. waxed two sides to 50 lb.		2	0	1	0
45 lb. waxed two sides to 65 lb.		3	0	1	0
80 lb. waxed two sides to 105 lb.		4	0	3	0
25 lb. coated one side with a flexible wax composition to 65 lb.	Wax up	5	3	5	4
	Wax down	4	3	5	4
25 lb. wax laminated (5 lb. wax) to 25 lb., thermoplastic coated	Coating up	3	0	0	0
	Coating down	1	0	0	0
Sulphites					
20 lb. dry waxed to 24 lb.		0	0	0	0
30 lb. dry waxed to 38 lb.		0	0	0	0
40 lb. dry waxed to 48 lb.		1	0	0	0
20 lb. unfilled, waxed two sides to 30 lb.		1	0	0	0
20 lb. filled, waxed two sides to 30 lb.		1	0	1	0
Manilla					
48 lb. waxed two sides to 67 lb.		3	0	2	0
Cellucine					
20 lb. waxed two sides to 25 lb.		1	0	1	0
Vegetable parchments					
27 lb.		1	1	1	1
40 lb.		2	1	1	1
27 lb. waxed one side to 34 lb.	Wax up	2	1	2	1
	Wax down	3	1	2	1
27 lb. waxed two sides to 33 lb.		1	1	2	1
'Greaseproof' papers					
20 lb. full-bleached		1	1	1	1
25 lb. full-bleached		1	1	1	1
30 lb. full-bleached		1	1	1	1
35 lb. full-bleached		1	1		
40 lb. full-bleached		3	1	2	1
25 lb. semibleached		1	1	1	1
25 lb. full-bleached, wet strength		1	1	2	1

TABLE I—*Concluded*

THE GREASE RESISTANCE OF SOME COMMON PACKAGING MATERIALS—*Concluded*

Material	Grease resistance score			
	Materials as received (average 15 determinations)		Materials aged one week at 140° F. (average 5 determinations)	
	Flat	Creased	Flat	Creased
Lard liners				
30 lb. full-bleached, semiplastic	3	2	3	1
40 lb. full-bleached	7	7	7	5
Shortening papers				
25 lb. superplastic	4	3	7	7
35 lb. superplastic	5	4	7	7
44 lb. superplastic	7	7	7	7
Glassines				
20 lb. full-bleached	5	3	5	5
25 lb. full-bleached	4	2	3	2
30 lb. full-bleached	6	1	4	3
40 lb. full-bleached	6	1	3	1
25 lb. full-bleached, opaque	2	1	1	1
40 lb. full-bleached, opaque	3	1	1	1
25 lb. full-bleached, opaque, plasticized	2	1	2	1
30 lb. full-bleached, plasticized	5	2	5	4
25 lb. semibleached	3	1	4	3
25 lb. red	3	3	3	3
25 lb. red, plasticized	1	1	3	2
20 lb. amber	3	1	3	3
25 lb. amber	2	1	3	1
30 lb. amber	4	2	4	2
25 lb. yellow	2	2	4	1
28 lb. yellow	3	1	4	1
25 lb. chocolate	1	1	3	2
25 lb. blue	3	3	4	3
25 lb. waxed two sides to 28 lb.	7	7	7	7
55 lb. wax laminated, bleached	7	7	7	7
25 lb. wax laminated to 25 lb. kraft	7	7	7	7
Cellophanes				
300 P.T.	7	7	7	7
300 M.S.T.	7	7	7	7
300 M.S.A.T.	7	7	7	7
300 M.S.Y.T.	7	7	7	7
Thermoplastics				
Polyethylene (0.003 in.)	6	6	6	6
Saran (0.002 in.)	7	7	7	7
Vinylite (0.002 in.)	7	7	7	7
Pliofilm (0.002 in.)	7	7	7	7
Cellulose acetate (0.002 in.)	7	7	7	7
Cellulose nitrate (0.003 in.)	7	7	7	7
Ethyl cellulose (0.005 in.)	7	7	7	7

None of the paraffin waxed kraft samples showed any grease resistance after folding. The kraft sample coated 40 lb. per ream with a flexible wax compound had a much greater transudation time than paraffin coated samples, and retained considerable resistance after folding. The sample of 60 lb. kraft, paraffin coated on one side to 72 lb., showed considerably greater grease resistance when the unwaxed side of the sheet was next to the turpentine; however for the sample coated with a flexible wax compound the opposite was true. The explanation for this is not apparent. Wax laminating two sheets of kraft effected no improvement in grease resistance after folding. Samples of paraffin waxed sulphite were no better than similar samples of waxed kraft.

While only one sample of each of manilla and cellucine were tested, paraffin waxed manilla had a resistance similar to that of waxed kraft, and waxed cellucine was little better than waxed kraft. Paraffin coated vegetable parchment required less wax than kraft paper to effect an improvement in grease resistance but, as with kraft, wax-coated vegetable parchment was no better than the unwaxed material after creasing. The results obtained with samples of paraffin coated vegetable parchment indicated that for a given weight of wax-coating, greater grease resistance could be achieved by putting all the wax on one side of the paper, rather than by dividing it between the two sides. Vegetable parchment, paraffin coated on one side, had greater resistance when the unwaxed side was toward the turpentine. Since paraffin coated kraft behaved in a similar manner it appears that papers coated on one side with paraffin should be used with the unwaxed side toward the greasy surface.

Application of a very light paraffin wax coating to glassine markedly improved its grease resistance both before and after creasing, and wax laminating glassine to glassine, or glassine to kraft, raised the grease resistance score far above that of either sheet alone. The results indicate that the more dense the base stocks, the more effective wax coatings become in enhancing the grease resistance of paper.

Ageing many materials at 140° F. markedly reduced their grease resistance. The major exceptions to this were Shortening papers and glassine, many samples of which had greater resistance to grease penetration after ageing. The resistance of creased samples of these stocks was markedly improved by ageing. When they were aged, much of the wax ran off the kraft samples that were coated with paraffin, and the material assumed the appearance of a dry waxed sheet. Ageing the kraft sample coated with a flexible wax compound did not lower the grease resistance score of the uncreased material, and creased samples had a greater resistance after ageing. The probable reason for this is that the temperature was not high enough to cause the wax to run off the paper, although it was sufficiently high to cause some of it to soak into the sheet. The vegetable parchments, greaseproof papers, Cellophanes, and thermoplastic films tested were not visibly affected by the high temperature storage.

Acknowledgments

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PACKAGING

VI. THE RELATIVE MERITS OF VARIOUS TYPES OF BAG CONSTRUCTION IN PRODUCING WATER-VAPOUR RESISTANT PACKAGES[1]

By C. G. Lavers[2]

Abstract

Water-vapour penetration was measured on pouch, flat, wedge, and square liner bags fabricated from Reynold's Metal A-51, 300 M.S.A.T. "Cellophane" coated 40 lb. per ream with a flexible wax composition, 55 lb. laminated bleached glassine, and 300 M.S.A.T. Cellophane. The bags were closed, where the material permitted, by heat-, glue-, and pressure-sealing, and by folding with or without tin-tie closures.

When Reynold's Metal A-51 or waxed Cellophane was used, excellent water-vapour resistance could be achieved with any of the bag types investigated, and a folded closure was as efficient as a heat-seal. With all materials except 300 M.S.A.T. Cellophane, bags made with glue were almost as good as those with heat-sealed construction. Unwaxed Cellophane or glassine provided more protection when the simpler forms of bags (pouch) were used. With unwaxed Cellophane, heat-sealing appeared to make a better liner than the use of glue, and a heat- or glue-sealed closure was superior to a double fold.

Introduction

An important factor in the packaging of many foods is the prevention of the passage of water-vapour either into or out of the package. Many flexible water-vapour barriers have been developed for this use. The water-vapour resistance of many of these barriers has already been assessed (1, 2), and it has been shown that, for products not likely to rupture the barrier, the best method of applying a water-vapour barrier is as a liner inside a carton (1). While the pouch type liner bag has generally been assumed to provide the greatest resistance to passage of water-vapour, little definite information is available on the relative merits of various types of bag construction. The purpose of this paper is to compare the water-vapour resistance of liner bags made in the basic commercial styles.

Materials and Methods

The names applied to various methods of forming bags are not constant from manufacturer to manufacturer, therefore the styles of bags tested and the names applied for the purpose of this study are illustrated in Fig. 1. The 'pouch' bag is the simplest to make, having only a seam at either side, and there is the least possible opportunity for water-vapour transmission through seams and seals. The 'flat' bag has two seams, one along the side, and another at the bottom; the junction of the side and bottom seams is a

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[2] *Chemical Engineer, Food Investigations.*

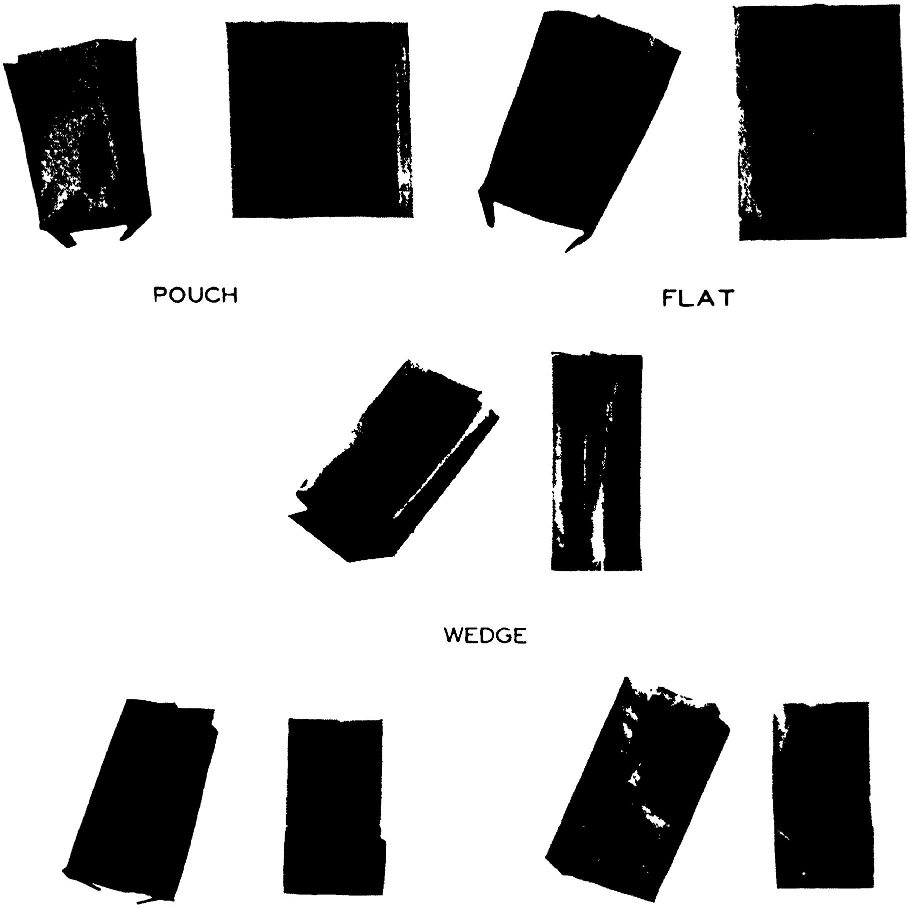

FIG. 1

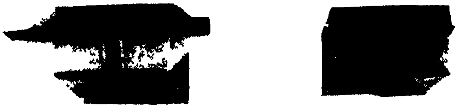

FIG. 2

FIG. 1. *Construction of the various types of bags studied.*
FIG. 2. *Some methods of closing bags used in this study.*

possible point of entry for water vapour. The 'wedge' type bag shown in Fig. 1 has a single side seam, gussets, and a wedge closure (Fig. 2) at the bottom. The additional folds in this type of bag might be expected to cause higher rates of water-vapour transmission in it than in the previous types. Glue-sealed 'square', or self-opening bags, shown in Fig. 1, were made with both the common grocery bag style of bottom, and with a 'flat' seal (Fig. 2) on the bottom. The flat bottom seal should improve the water-vapour resistance of this type of bag over that of the wedge style of bag unless the material used is sensitive to the added creasing required to make it square when opened. Square bags made using heat-sealed construction were necessarily of the flat bottom closure style.

Besides the closures illustrated in Fig. 2, unsealed single and double fold closures, some with and some without a tin-tie were tested. When folded closures are used special care must be taken to see that the box is well filled so the top of the carton will prevent the fold from opening. In the course of the study, pressure sealed bags were also examined. Only heavily waxed material could be used for this purpose. All seams were heat-sealed except the final closure, which was made by running a dull pencil point across the mouth of the bag, causing the waxed surfaces to stick together.

Four materials with various characteristics were used to make the liners for this investigation. These were: Reynold's Metal A-51 (kraft paper laminated to metal foil coated with Butvar), 300 M.S.A.T. "Cellophane" coated 40 lb. per ream with a flexible wax composition, 55 lb. laminated bleached glassine (coated on one side with a heat sealing composition), and 300 M.S.A.T. Cellophane. When Reynold's Metal A-51 was used to make glue-sealed bags it was necessary to reverse the material and place the kraft on the inside of the bag and the heat-sealing surface outside.

The combinations of materials, bag styles, and closures tested are given in Table I.

The method of measuring water-vapour transmission was the same as that used in a previous investigation (1). The materials were fabricated into liners of suitable size to fit inside a light chipboard carton, 4 by $2\frac{3}{4}$ by $1\frac{5}{16}$ in. (opening end, $2\frac{3}{4}$ by $1\frac{15}{16}$ in.). The liner was opened, inserted into a carton, and partially filled with sawdust; then 73.5 gm. of anhydrous calcium chloride in a perforated P.T. Cellophane bag was added; this bag was surrounded by sawdust and the remainder of the liner was filled with sawdust; the liner and carton were then closed. Six filled packages were used to test each type of liner bag, and six packages without calcium chloride and sawdust were used to estimate the sorption of water-vapour by the packaging materials. The filled packages and dummies were placed in a cabinet operating at 95° F. and 100% relative humidity (vapour-pressure differential, approximately 42 mm. of mercury), and moisture gain was determined by weighing each package at weekly intervals for four weeks.

TABLE I

WATER-VAPOUR TRANSMISSION (GM. PER WEEK) OF VARIOUS TYPES OF LINER BAGS

(Standard error for mean transmission rates, 0.32 gm. per week)

Construction and type of bag	Closure	Packaging material			
		Reynold's Metal A-51	300 M.S.A.T. Cellophane coated 40 lb./ream wax composition	55 Lb. laminated bleached glassine, coated with a heat-sealing composition	300 M.S.A.T. Cellophane
Glue-sealed	Glue-sealed				
Pouch	Flat	0.26	—	1.29	2.86
Flat	Flat	0.22	—	1.98	4.91
Wedge	Wedge	0.26	—	1.75	5.78
Square, bottom sealed as for flat bag	Wedge	0.22	—	2.25	3.74
Square, bottom sealed as in a grocery bag	Wedge	—	—	2.33	3.74
Heat-sealed	Heat-sealed				
Pouch	Flat	0.0	0.29	1.24	1.46
Flat	Flat	0.17	0.47	1.39	2.53
Wedge	Wedge	0.34	0.43	1.70	2.78
Square, bottom sealed as for flat bag	Flat	0.0	0.44	3.43	3.78
	Wedge	0.0	0.83	2.92	4.16
	Unsealed				
Pouch	Single fold, tin-tie	0.0	—	—	—
	Double fold, tin-tie	0.0	—	—	—
Square, bottom sealed as for flat bag	Double fold, flat	0.19	0.53	3.24	4.68
	Double fold, wedge	0.21	0.82	3.10	4.69
	Pressure sealed				
	Double fold, flat	—	0.60	—	—
	Double fold, wedge	—	0.56	—	—
	Single fold, flat	—	0.62	—	—

Results

Water-vapour transmission rates of the various types of bags tested are shown in Table I. These values were calculated by the method used in a previous study (1). The standard error for the mean transmission rates reported in the present study was of the same order of magnitude for all the different bag types. The average standard error was 0.32 gm. per week. For all types of bags the protection provided by the different materials in decreasing order of efficiency was: Reynold's Metal A-51, 300 M.S.A.T. Cellophane wax-coated 40 lb. per ream, 55 lb. laminated bleached glassine, and 300 M.S.A.T. Cellophane. This agrees with results obtained in a previous study (1).

The various types of liner bags made from Reynold's Metal A-51 did not differ significantly in behaviour. However, the transmission of glue-sealed bags was generally slightly higher than that of those made with heat-sealed construction, and the heat-sealed wedge bag appeared slightly inferior to the other types. The water-vapour transmission of unsealed bags (folded closures), with or without a tin-tie, did not differ markedly from that of bags that were heat-sealed, but the addition of the tin-tie to a folded closure improved the water-vapour resistance somewhat.

Although no significant differences occurred in the water-vapour resistances of the various types of bags made of wax-coated Cellophane, the pouch type bag appeared to be slightly superior. Little difference in transmission was expected between types made with this material because the heavy wax coating when melted in the heat-sealing operation would flow into places around folds in the seal that might be left open when other materials are used. Unsealed folded closures were as good as those that received the added treatment of pressure sealing. This would probably not be true, however, if the fold was not held closed by the outer carton.

For any one type of bag little difference was noted between glue- and heat-sealed construction with liners made of laminated glassine. There was, however, a tendency for the efficiency of the bag to decrease as the complexity of construction increased, i.e., from pouch to flat to wedge to square. This was attributed to the combined effect of increased difficulty in sealing and the added folding of the material required in making the more complex bags. Glassine, being a relatively brittle material, develops pinholes easily when folded. Square, glue-sealed liners with the bottom sealed as in a grocery bag were as good as those with a flat seal on the bottom; and the water-vapour resistance of bags with a folded closure was equal to that of bags closed by heat-sealing.

Unlike the bags made of laminated glassine, heat-sealed Cellophane bags in the pouch, flat, and wedge styles were superior to those made with glue. This was probably due to the greater spring-back that occurs when Cellophane is folded. Cellophane is a very thin material, not readily creased, and it is difficult to obtain a perfect glue-seal (especially at corners) unless true surfaces are used to hold the material in place until such time as the glue has set. As with glassine, the more complex types of bags, whether heat- or glue-sealed, were generally less efficient water-vapour barriers. Equal protection was provided by square, glue-sealed bags with grocery or flat style bottoms. Folded closures on Cellophane bags were inferior to heat seals, likely because the thin springy nature of this material caused some opening of the fold even though the bags were well filled and held shut by the outer container.

Discussion

When the results in Table I are considered, it must be remembered that all bags were carefully made in the laboratory, and great care would be required to produce bags of equal quality on a commercial scale. For example, a square bag with a grocery type bottom as used in this experiment would be sealed more completely than the same product from most bag making machines at present in use. However, once the plant process has been perfected it should be possible to make bags in any style superior to those used in this study. Nevertheless the results given here should represent the relative effectiveness of the various bag types, materials, and closures.

Fairly heavy materials, like Reynold's Metal A-51, and heavily waxed sheets (flexible wax composition) that are not sensitive to creasing can be formed into bags with high water-vapour resistance regardless of the type of bag used, and a folded closure can be as efficient as a heat-seal. However, materials that are sensitive to creasing, such as glassine, are best utilized for only the simpler types of bags. With materials like Reynold's Metal and glassine, bags sealed with glue are almost as good as those made with heat-sealed construction.

Thin springy materials, like unwaxed Cellophane, provide more water-vapour resistance when the simpler forms of bags (pouch) are used, and a heat- or glue-sealed closure is superior to a double fold. Heat-sealing rather than the use of glue appears to make a better liner with this packaging material.

The above results indicate that it is generally desirable to keep bag construction as simple as possible if the most protection from loss or gain of water vapour is to be expected. However, the bags of simple construction are often more difficult to use in small scale commercial or home operations. For these uses, the more complex bags may be satisfactory for packaging many products provided suitable materials are employed.

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DRIED MILK POWDER

VII. THE EFFECT OF SEASON OF PRODUCTION ON KEEPING QUALITY[1]

By Jesse A. Pearce[2] and W. A. Bryce[2]

Abstract

Milk powders of 1% butterfat content, produced in the fall of the year, had higher initial palatability scores than similar powders prepared in the spring. The skim milk powders from fall milk decreased in quality throughout a storage period of 16 wk. at temperatures of 80°, 100°, or 120° F. Similar powders from spring milk stored at 80° F. increased in quality throughout the storage period while those stored at 100° and 120° F. first increased and then decreased in quality. Powders of 26 or 28% butterfat, produced in the spring or in the fall, had equal initial palatability scores and when stored deteriorated equally. Fall milk powder containing 30% butterfat was better initially than the comparable spring sample, but, when stored, quality changes in both types were about equal. At each storage temperature all whole milk powders deteriorated at about the same rate.

Introduction

In conjunction with investigations of some of the factors affecting deterioration of milk powder, e.g., cooling subsequent to drying (5), exposure to light (6), storage temperature (1), method of packing (7, 11), moisture content (1), and producer (1), it was deemed advisable to evaluate the difference in the behaviour of milk powder produced at different seasons of the year.

It has been shown that liquid milk obtained during the fall and winter months has a higher solids content than spring and summer milk (2, pp. 29-31; 4, p. 405; 10, pp. 55-61), that spring milk is poorest in fat and fall milk the richest (2, 10) and that the fat of milk produced in the fall of the year, when good pasture is no longer available, has a lower iodine value than the fat of spring milk (3). It would be expected, therefore, that fall milk, when dried, would be more stable than powder produced in the spring. This paper describes the results of a storage study on samples of spring and fall milk powders of different fat levels but of equal moisture contents.

Materials and Methods

The spring and fall milk powders used in this experiment were spray-dried and were produced during the latter part of May and early in December, 1944. The butterfat levels compared were 1, 26, 28, and 30%. The moisture content of the powders was adjusted to 2% before packing in tin-plate containers with air as the headspace gas. The palatability of the powders was determined initially and after 2, 4, 8, and 16 wk. storage periods at temperatures of 80°,

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100°, and 120° F. (27°, 38°, and 49° C.). In assessing the quality of the powders, samples were reconstituted as previously described (5) and palatability was assessed by 14 tasters. Scoring was done on a scale of 10 (the equivalent of excellent fresh whole or skim milk) to 0 (a repulsive specimen). A score of 4 is usually considered the point at which milk powder is no longer suitable for use as a milk drink. The reliability of the scoring by the taste panel has been estimated and palatability assessment was found to be more suitable than any of the chemical tests of milk powder quality (5).

Results

The data for the 4, 8, and 16 wk. samplings were assessed by an analysis of variance with the results shown in Table I. This table shows that no constant difference could be attributed to the use of either spring or fall milk in powder production. The difference between samples was attributed to the inclusion of data for skim milk powder in the comparison. Skim milk powders are generally considered to be of poorer quality, when reconstituted as a milk drink, than whole milk powders. The significant effects of storage temperature and storage time have been discussed in earlier papers, and the other factors of significance can be explained by referring to Fig. 1.

TABLE I

ANALYSIS OF VARIANCE OF PALATABILITY DATA ON STORED POWDERS PREPARED FROM SPRING AND FALL MILK

Variance attributable to:	Degrees of Freedom	Mean square
Seasons	1	1.15
Samples	3	1.12*
Temperature	2	15.30**
Storage time	2	11.93**
Seasons × samples	3	2.45**
Seasons × temperature	2	1.45*
Seasons × time	2	3.83**
Samples × temperature	6	0.25
Samples × time	6	0.83*
Temperature × time	4	1.28*
Residual	40	0.35

* *Exceeds the 5% level of statistical significance.*
** *Exceeds the 1% level of statistical significance.*

As shown in Fig. 1, skim milk powder (1% fat) from fall milk had a higher initial palatability than skim milk powder from spring milk but decreased in palatability during storage at all temperatures, while the palatability score of skim milk powders from spring milk first increased, then decreased during storage at 100° and 120° F., but at 80° F. increased throughout the storage period. It is of interest to note that in previous studies, all skim milk samples exhibiting low initial palatability and increasing palatability during storage have been produced in the spring of the year (5, 6, 7) while the only other general decrease similar to that observed in this study was in a powder produced from fall milk (6). The possibility that this difference in behaviour was attributable to plant practice seems unlikely since powders produced in the spring by two different companies exhibited parallel behaviour (1).

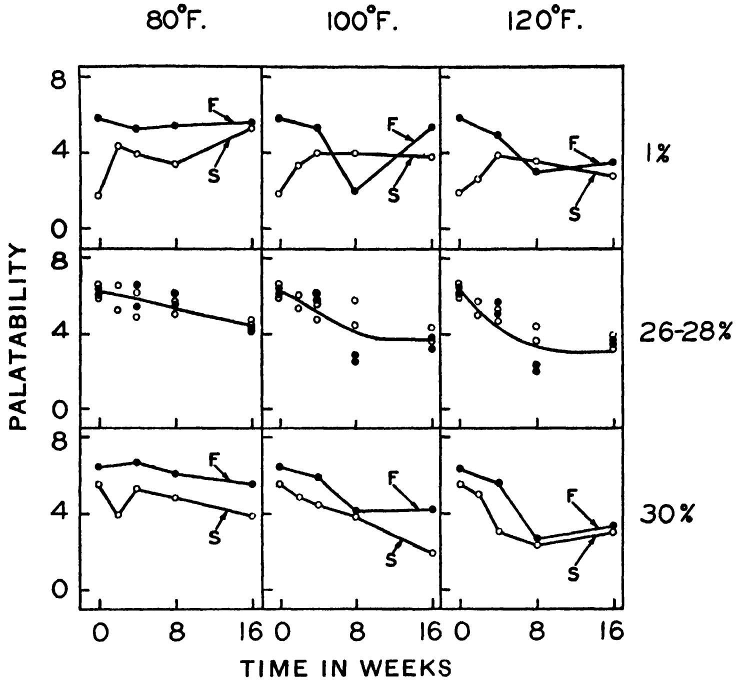

FIG. 1. *The decrease in palatability of stored milk powders prepared from spring and fall milk.*

Whole milk powders having 26 or 28% fat, and prepared from milk produced in the spring or in the fall, did not differ from each other in keeping quality. However, fall milk powder with 30% butterfat had a higher initial palatability than the comparable spring sample. The high-fat, spring powder had a lower palatability than any of the other whole milk powders. This difference may be attributable to some variation in plant practice. Deterioration in both 30% butterfat powders occurred at about the same rate. Deterioration in all whole milk powders showed comparable trends at the same storage temperatures. Changes in whole milk powders were different from those in the skim milk powder from spring milk, but were similar to, although slightly more rapid than, the changes in skim milk powder from fall milk.

Discussion

Experimental work on milk in Finland (10) has shown an increase in fat and protein of milk produced during the summer months and an increase in lactose of that produced during the winter months. Since the change in composition of milk as cows go to pasture, and vice versa, is not abrupt, it might be expected that the lactose–protein ratio in May would be higher than the ratio in December milk. Calculations on American data (6) show that, for Jersey cows, the ratio of lactose to protein in May is 1.42 compared with about 1.15 for November and December. This makes a difference of 2.5 to 3% in the lactose content of spring and fall dried whole milk and about 4% difference in the lactose content of spring and fall skim milk powders. This, when considered in relation to the high drying temperatures used in preparing skim powders, makes possible some explanation of the difference in behaviour of spring and fall skim milk.

It has been shown that the addition of lactose to a partially defatted milk prior to drying provided some protection to the product during storage (8). However, it is known that lactose deteriorates rapidly when subjected to heat. Spring milk powder might, therefore, have more volatile breakdown products from lactose decomposition during drying than fall milk powder. As suggested previously (6), these degradation products may be dissipated as a result of the repacking operation or of chemical recombination during storage to form substances that do not possess disagreeable flavours. As storage proceeds, the undesirable degradation products would diminish and the preservative effect of the higher lactose content of the spring skim milk powder would become noticeable.

Milk fat from cattle on pasture differs in degree of unsaturation from the fat of milk from partially stall-fed animals (4). If the milks used here conformed in unsaturation to English milks, it would be expected that the butterfat in the fall milk would have an iodine value about six lower than the butterfat in the spring milk. Fall milk powder, then, should be more stable than spring milk powder. Some reflection of this increased stability may have been shown by the higher palatability of the fall milk powder containing 30% fat. However, the deterioration noted in powders of 26 and 28% fat contradicted this and indicated that the butterfat at both seasons was equally susceptible to deterioration.

The facts that packing in inert gases affords only partial protection to whole milk powder (7), that light exerts a harmful effect on skim milk powder (7), and that almost equal deterioration occurred in some whole and skim milk powders point to solids-not-fat as an important factor in milk powder deterioration. The observation that milk powders containing 50 to 55% fat keep 15 to 18 months while powders with 5 to 6% keep only about four months (9) supports this assumption.

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PRESERVATION OF EGGS

V. METHODS FOR DETERMINING YOLK INDEX[1]

By N. E. Gibbons[2]

Abstract

Breaking out the egg on a glass plate and measuring the height and width of the yolk in position in the white is a rapid and easy method of determining yolk index. The correlation coefficient between this method and one of the more laborious methods, in which the white is removed, is 97. The prediction equation is $y = -0\ 001 + 0\ 9172x$.

Introduction

The use of the yolk index as a measure of egg quality was first proposed by Sharp and Powell (3). In their method, the yolk was completely freed of all the white. To remove the last traces of adhering albumen, the yolk was held in the palm of the hand and wiped gently with a cloth. It was then placed on a glass plate, the diameter and height measured, and the yolk index calculated by dividing the latter value by the former. After being placed on the glass plate the yolk continued to flatten for a considerable length of time, but this flattening was most rapid during the first 60 min. However, it was possible to obtain reasonably accurate information if the measurements were made after the yolk had been standing for five minutes. When determining the yolk index by this method, the chances of breaking the yolk are obviously high, especially when storage eggs are used.

The method was modified by Smith (4, pp. 60-61) who left the adherent film of white. This involved less handling and less risk of damage It was also suggested that the value obtained with the white adhering was of more interest as a basis for judgment of quality. A standard period of two minutes was allowed to elapse before measurements were made.

Further modifications were made at the Low Temperature Research Station at Cambridge (1). As, in this study, comparisons were made with this method it is given in detail: the shell is cracked round by means of a knife or scalpel and the contents carefully transferred to an egg separator. As soon as the major portion of the thick fraction of the white has passed through the opening of the separator, the yolk is allowed to slide into a glass dish containing a sugar solution isotonic with the yolk, i.e., 10.4 gm. of sucrose per 100 gm. of water. While in this sucrose solution the remainder of the thick white and chalazae are removed. The yolk is then placed on a level glass plate, covered with a small beaker or crystallizing dish and allowed to settle for three minutes. The height of the yolk is then determined with a depth micrometer and the width measured across the long and short axes. The index is expressed as the height divided by the mean width.

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In the N.R.C. laboratories it has been the practice to break out the egg onto a glass plate and measure the height and width of the yolk as it rests on the white (2). Practically the yolk is never considered without the white and as the support given by the albumen lessens with time, as does the strength of the yolk membrane, it seems reasonable to measure the yolk in this position. Furthermore the above methods are time-consuming and too often considerable time and material are wasted because the yolk breaks at the last moment. To test the validity of the N.R.C. method a comparison was made between it and the method used at the Low Temperature Research Station.

The N.R.C. method is as follows. The egg is broken out onto a clean level glass plate and the yolk diameter measured immediately with calipers along the axis bisecting the short and long diameters. The yolk height is then measured with a spherometer. These two measurements are completed within 30 to 40 sec. of breaking the egg.

Experimental

For comparison, the yolk indices of 182 eggs of various grades and storage histories were determined first by the N.R.C. method and then by the L.T.R.S. method. The scatter diagram and regression line are shown in Fig. 1. The

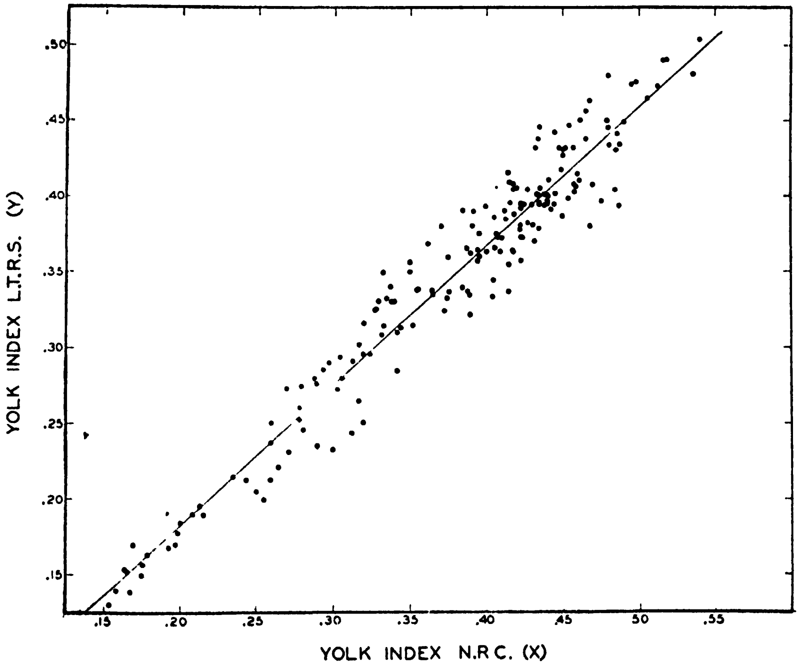

FIG. 1. *Relation between yolk indices determined by N.R.C. method and the method used by Low Temperature Research Station.*

correlation coefficient between the two sets of values is .97. The prediction equation is $y = -0.001 + 0.9172x$. The N.R.C. method therefore gives practically the same results as the longer method, and the losses from breakage are negligible.

As may be seen from the regression line the present method gives slightly higher values than the L.T.R.S. method. The white under the yolk contributes slightly to this but the effect decreases as the white thins (Table I). This was shown by breaking the eggs out on a cold brass plate, taking the

TABLE I

EFFECT OF AMOUNT OF WHITE UNDER YOLK ON YOLK INDEX WHEN MEASURED BY N.R.C. METHOD

——	Yolk diameter, in.	Yolk height, in.	Yolk index	Height of white under yolk, in.	Corrected yolk height, in.	Corrected yolk index
Fresh eggs	1.67	.840	.503	.028	.812	.486
	1.68	.780	.464	.017	.763	.454
	1.74	.870	.500	.030	.840	.483
	1.69	.775	.458	.030	.745	.441
	1.70	.730	.429	.031	.699	.411
	1.78	.792	.444	.020	.772	.434
	1.65	.798	.484	.032	.766	.464
	1.69	.877	.519	.038	.839	.496
	1.64	.765	.466	.035	.730	.445
	1.62	.869	.536	.025	.844	.521
Average	1.69	.810	.480	.029	.781	.464
Commercial Grade *C*	1.63	.695	.430	.025	.670	.411
	1.67	.721	.432	.040	.681	.407
	1.71	.752	.440	.025	.727	.425
	1.82	.645	.354	.018	.627	.344
	1.61	.686	.426	.007	.679	.422
	1.70	.679	.399	.024	.655	.385
	1.69	.783	.463	.029	.754	.446
	1.82	.815	.448	.040	.775	.426
	1 68	.695	.414	.022	.673	.401
	1.65	.722	.438	.031	.691	.419
Average	1.70	.719	.424	.026	.693	.409
Experimental eggs stored at 70° F.	1.98	.397	.201	.002	.395	.199
	1.82	.585	.321	.011	.574	.315
	1.70	.631	.371	.008	.623	.366
	1.89	.540	.285	.011	.529	.280
	1.76	.602	.342	.001	.601	.341
	1.77	.571	.322	.006	.565	.319
	1.81	.512	.283	.001	.511	.282
	1.78	.605	.340	.006	.599	.336
	1.78	.535	.300	.003	.532	.299
	1.80	.617	.343	.017	.600	.333
Average	1.81	.560	.311	.007	.553	.307

usual measurements, and then placing the plate over a steam jet. The albumen was quickly coagulated, the yolk removed, and the thickness of the albumen measured.

The flattening of the yolk due to the removal of the supporting albumen should also reduce the yolk index. The differences in yolk index of 60 eggs, as determined by the two methods, ranged from 0.066 to 0.020, and this flattening may contribute the greater part of the difference. The effect of both the white under the yolk and the removal of the supporting albumen decreases as the quality of the egg decreases. This is evident from the slope of the regression line.

Acknowledgments

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THE EFFECT OF METHOD OF COOKING ON THE MOISTURE CONTENT OF CANNED PRE-COOKED POULTRY MEAT[1]

By D. MacDougall[2] and N. E. Gibbons[3]

Abstract

Moisture content of the meat and solid content of the broth from open- and pressure-cooked chicken and fowl were investigated during cooking and subsequent processing. During cooking, pressure-cooked meat lost more moisture than open-cooked meat, but during canning and separating the reverse was true. For these reasons, approximately 4 oz. of open-cooked meat, as compared with 3.6 oz. of pressure-cooked meat, must be canned to obtain 3.5 oz. of meat in the finished product. During cooking there was a greater loss of moisture from dark than from light meat. Under all the cooking conditions used the loss of weight from fowl during processing and separation was greater than that from chicken meat. The loss in weight of meat during canning and processing is mainly due to moisture changes rather than the loss of solids.

Introduction

Canadian regulations (1) state that canned poultry to be sold as 'jellied pack' must have a solid meat content of not more than 55% and not less than 50% of the final pack. Poultry canners who used the open-cook method were originally led to believe that, if $3\frac{1}{2}$ oz. of solid meat were to be obtained from a 7-oz. can after retorting and separating, it was necessary to place $3\frac{3}{4}$ oz. of cooked meat in the can. Both canners and poultry inspectors found that the loss of weight with open-cooked meat was greater than allowed for by the above limits. On the other hand with pressure-cooked meat there was little difficulty in meeting the requirements. Therefore, it was decided to investigate the moisture relations of poultry meat throughout the usual canning operation. Both chicken and fowl were studied and the light and dark meat were treated separately. Moisture content of the meat and solid content of the broth before and after the various heat treatments involved were investigated.

Experimental Procedure

Moisture was determined by cutting a sample of meat into a weighed aluminum drying dish, placing this in an air oven at 100° C. for two hours, and finally drying to constant weight *in vacuo* at 100° C. A period of 16 hr. in the vacuum oven was shown to be sufficient time for samples to reach constant weight and therefore this drying time was used throughout the experiment. The solid content of the broth was determined by drying the sample to constant weight in a small beaker in the air oven at 100° C.

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To investigate sampling technique, the moisture content of various muscles of dressed chickens was determined. The pectoral, leg, and wing muscles were dissected from two birds and their moisture contents were recorded. It was concluded (Table I) that the moisture content of a single muscle or a portion of a muscle, on either side, could be used as an index of the moisture content of the meat of a whole bird.

TABLE I

MOISTURE CONTENT OF VARIOUS MUSCLES OF DRESSED CHICKEN

Chicken	Muscle	Moisture, %	
		Left	Right
A	Outer pectoral	74.0	74.3
	Inner pectoral	73.5	73.9
	Wing	74.5	74.5
	Leg	74.4	74.1
B	Outer pectoral	72.8	72.7
	Inner pectoral	72.8	72.6
	Wing	73.3	73.4
	Leg	71.4	71.0

In the main experiment, three open and three pressure cooks, using four birds in each, were carried out on both chicken and fowl, which were cooked separately. The open cooks were made in a steam-jacketed kettle with the steam outlet from the central chamber open, giving an internal temperature of 100° C. (212° F.). In these cooks approximately one litre of water was used for each 5 lb. of bird. The times were 50, 75, and 100 min. The pressure cooks were done in the same kettle for 20, 30, and 40 min. at 121° C. (250° F., 15 lb. steam pressure). The times were chosen in each case to give under-, normal-, and overcooked meat. Before cooking, all birds were tagged and a portion of the outer pectoral muscle was removed to determine the moisture content of the light meat and a portion of either the gastrocnemius or biceps femoris muscle was taken for the moisture determination of the dark meat. After cooking, portions of the corresponding muscles on the opposite side of each bird were removed and their moisture contents determined.

After sampling, the cooked meat was stripped from the bones and 3½-oz. portions were weighed into 7-oz. cans. Light and dark meat were canned separately. The broth from each cook was defatted, adjusted to a sp. gr. of 1.000 and 1.010 at 50° C. (122° F.) for open- and pressure-cooked meats, respectively, and 2.0% Irish moss gelose was added as a jelling agent along with 4% salt according to the regulations for the packing, grading, and marking of canned poultry (1). When broth samples had been taken for solids determinations, 3½-oz. portions of broth were poured over the meat and the cans were preheated and sealed. All cans were retorted for one hour at 116° C. (240° F.).

Two types of separation apparatus were available, the type described by Reedman (2) and a modification of this apparatus (Fig. 1) designed by Mr. T. A. Steeves, formerly of these laboratories. The rate of heat penetration into the apparatus was determined using copper–constantan thermocouples. A period of 30 to 40 min. in the autoclave was necessary to raise the meat and jelly inside the separator to 100° C. Accordingly, all separations were made at 121° C. for 45 min. To compare the efficacy of the two types of apparatus, duplicate sets of canned chicken were run in each type.

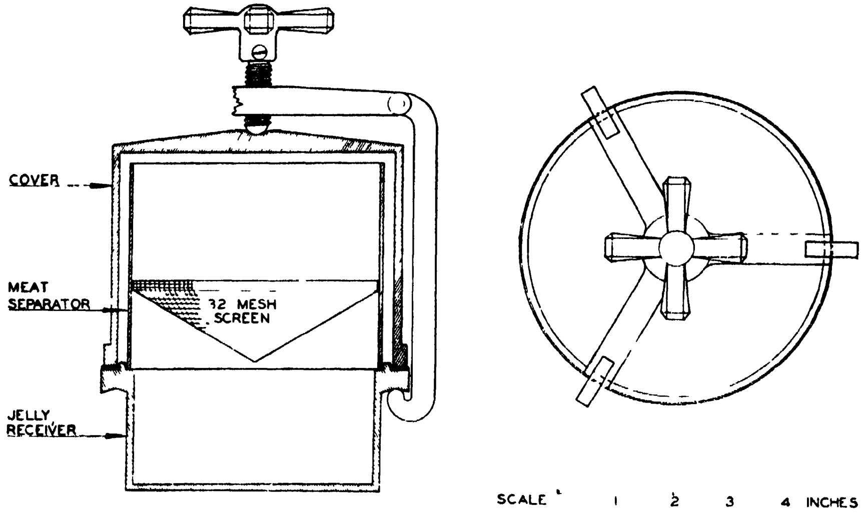

FIG. 1. *Modified separation apparatus for canned poultry.*

Since some of the loss of moisture was attributed to the method of separating the meat and jelly, an attempt was made to determine the actual moisture loss due to the separation procedure. However, since it was not possible to separate the meat and jelly completely by means other than heat, no conclusive results were obtained.

Since it is commercial practice in open cooking to cover the birds completely with water and to do several cooks in the same broth, the experiment was repeated in this way. All determinations were carried out as before and, in order to have a valid check, pressure cooks were carried out on birds obtained from the same source. In the open cooks it was necessary to add eight litres of water to cover four birds completely. This was brought back up to volume after each cook. Agar (1%) was used as the gelling agent in this test.

All results were subjected to statistical analysis.

Results

Moisture Changes in Meat

Average moisture losses from chicken and fowl during cooking and the canning and separation procedures are shown in Table II. Necessary differ-

TABLE II

LOSS OF ORIGINAL MOISTURE FROM POULTRY MEAT DURING COOKING AND CANNING

Treatment	Average percentage loss during cooking	Average percentage loss due to cooking, and to canning and separating	Average percentage loss due to canning and separating
Chicken			
Open cook			
50 min.	13.9*	16.5	2.6
75 min.	17.4	17.4	0.0
100 min.	14.1	16.6	2.5
Pressure cook			
20 min.	19.9	21.6	1.7
30 min.	18.8	18.9	0.1
40 min.	21.6	21.4	−0.2
Necessary difference (5%)	2.5	1.8	3.1
Fowl			
Open cook			
50 min.	12.1**	20.0	7.9
75 min.	13.8	18.3	4.5
100 min.	14.4	17.8	3.4
Pressure cook			
20 min.	18.7	19.0	0.3
30 min.	19.8	19.2	−0.6
40 min.	18.8	17.7	−1.1
Necessary difference (5%)	1.4	2.6	2.9

* *Means of 16 observations.*
** *Means of 8 observations.*

ences for a 5% level of significance are also given. Moisture losses are calculated throughout on the basis of the original weight of raw meat.

These results show that pressure cooking removes a significantly greater amount of the original moisture from both chicken and fowl meat than does open cooking. The only significant effect of time of cooking noted was with the short time open cook on fowl. Here the loss of moisture was significantly less than for either of the longer cooks.

The data obtained with chicken meat after separation show the same general effects as those obtained after cooking; the total moisture loss was significantly greater from the pressure-cooked than from the open-cooked meat. However, the loss due to canning and separating was greater for the open than for pressure-cooked meat, but time of cooking had little effect. Canning and separation after pressure cooking caused the greatest loss in meat that was cooked for 20 min. only. With the fowl meat, canning and separation eliminated any difference in moisture due to method of cooking since the moisture loss attributable to canning and separation was much greater in the open- than the pressure-cooked meat and in each instance was inversely proportional to the time of cooking. There are indications that after canning, over-cooked meat may reabsorb some moisture.

The percentage losses of original moisture from both light and dark meat are compared in Table III. It is evident that dark meat lost, significantly more moisture than light meat, the difference being greater in open than in pressure cooking. These differences persisted even after processing and separation. Although the results are not presented, similar differences were noted with fowl meat.

TABLE III

PERCENTAGE OF ORIGINAL MOISTURE LOST FROM LIGHT AND DARK CHICKEN MEAT DURING COOKING AND PROCESSING

(Means of 12 observations)

Treatment	Type of meat	Percentage loss of original moisture during cooking	Percentage loss of original moisture after separation	
			Old separator	New separator
Open cook	Light	11.2	15.7	13.5
	Dark	19.1	19.8	18.4
Pressure cook	Light	18.5	19.9	18.2
	Dark	21.7	22.6	21.8
Necessary difference (5%)		2.5	1.4	1.4

Comparison of the results obtained with the two types of separation apparatus show that the older type dried out the meat considerably more than did the newer one.

TABLE IV

WEIGHT OF MEAT OBTAINED AFTER SEPARATION (ORIGINAL WEIGHTS, 3.50 OZ.)

Treatment	Chicken, oz.	Fowl, oz.
Open cook		
50 min.	3.05*	2.67**
75 min.	3.06	2.88
100 min.	3.16	3.04
Pressure cook		
20 min.	3.27	3.10
30 min.	3.44	3.37
40 min.	3.46	3.29
Necessary difference (5%)	0.17	0.17

* *Means of 16 observations.*

** *Means of 8 observations.*

The average weights of meat obtained after separation are contained in Table IV. These results confirm those obtained in the moisture studies. It will be noted that method has a much greater effect than time of cooking on the weight of meat obtained. In addition, the loss from fowl meat was greater than that from chicken meat for all cooking conditions. There were no significant effects of cooking time with the open-cooked chicken. With pressure-cooked chicken the loss from meat cooked 20 min. was greater than from meat cooked for the longer times. This difference just reaches the 5% level of significance. There was a significantly greater loss of weight from the fowl cooked 20 min. than from fowl that received the longer cooks and that had been dehydrated to a greater extent during the cooking process. It should also be mentioned that there was a significant difference between the weights of light and dark meat obtained after separation from fowl but not from chicken.

As the changes in percentage of solid material in the broth after canning and separating were relatively small and there were no significant differences between cooks, these results have not been included. However, it should be

TABLE V

LOSS IN WEIGHT (OZ.) FROM CANNED CHICKEN AND FOWL DURING CANNING AND SEPARATING, TOGETHER WITH ESTIMATES OF THE WEIGHT OF COOKED MEAT NEEDED TO OBTAIN 3½ OZ. AFTER CANNING AND SEPARATING

Treatment	Average moisture loss	Average solids loss	Combined loss	Total observed loss	Calculated weight to obtain 3.5 oz. after canning and separation
Chicken					
Open cook					
50 min.	0.34	0.07	0.41	0.45*	4.0
75 min.	0.26	0.08	0.34	0.44	4.0
100 min.	0.28	0.03	0.31	0.34	3.9
Pressure cook					
20 min.	0.18	0.07	0.25	0.23	3.7
30 min.	0.04	0 05	0.09	0.06	3.6
40 min.	0.02	0.05	0.07	0.04	3.5
Fowl					
Open cook					
50 min.	0.71	0.14	0.85	0.83**	4.6
75 min.	0.48	0.14	0.62	0.62	4.3
100 min.	0.36	0.13	0.49	0.46	4.0
Pressure cook					
20 min.	0.27	0.13	0.40	0.40	4.0
30 min.	0.12	0.01	0.13	0.13	3.6
40 min.	0.16	0.06	0.22	0.21	3.6

* *Means of 16 observations.*

** *Means of 8 observations.*

noted that there was a greater, but not significant, loss of solid material to the broth from dark than from light meat.

The entire experiment is summarized in Table V. In this the average losses of both moisture and solids are presented together with the total observed loss in weight. In calculating the loss of solid material to the broth it was assumed that the dry weight lost by the meat in the canning and separation processes was gained by the broth. The principal loss of weight was due to moisture and not to solid material. The contrast between the results for chicken and those for fowl should be especially noted. For every cooking condition used the meat obtained from fowl showed a greater decrease in weight on subsequent processing than did that obtained from chicken. It can be seen from these results that if a can of chicken that has been open cooked is to contain 50% by weight of meat after separation, it must contain about 60% of meat initially. The final column of Table V gives an estimate of the weights of precooked meat that must be canned if 3½ oz. are to be obtained after autoclaving and separation.

Acknowledgments

The authors are indebted to Mrs. R. Michael, Mrs. U. Irish, Mr. John Francis, and Miss Edna Birchard for technical assistance and to Mr. T. A Steeves for permission to include the design of the separation apparatus.

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PRECISION OF ASSESSMENT OF PALATABILITY OF FOODSTUFFS BY LABORATORY PANELS

II. SALTINESS OF BACON[1]

By J. W. Hopkins[2]

Abstract

Numerical ratings of the salty taste of freshly cooked portions of 80 pieces of Wiltshire-cured Canadian bacon by each member of a panel of 23 judges are analysed statistically, with results in general qualitative agreement with those previously reported for other palatability tests made in the same laboratory. Single assessments were subject to considerable random variation superimposed upon wide differences between individuals in respect of both tolerance and sensitivity. Nevertheless, a significant element of correlation made possible reproducible results, although it is calculated that to discriminate differences of the order of 5% on the organoleptic scale would have required 35 and 62 judges for intra- and inter-panel comparisons, respectively. The preferred degree of saltiness corresponded to a sodium chloride content of the cooked bacon of about 4¾% in the absence, and of roughly 4% in the presence of 2½ parts per thousand of sodium nitrate.

Introduction

In an earlier paper (3) the writer distinguished between 'grading' (absolute) and 'analytical' (relative) assessments of the palatability of foodstuffs by panels of judges, and described the results of statistical analyses of ratings of butter, dried eggs, dried milk, and ration biscuits made in these laboratories. These analyses included a numerical investigation of the judging characteristics of individuals by computation of the correlation coefficients and regression equations relating their assessments to the average of those of all other members of the same panels. A parallel study has since been made of assessments of the saltiness of cooked bacon, the outcome of which is reported now.

Data

Data for this study consisted of numerical ratings of the saltiness of freshly cooked portions of 80 different pieces of Wiltshire-cured Canadian bacon by each member of a panel of 23 judges, 17 male and 6 female, recruited from the scientific, technical, and administrative staff of the Divisional laboratories. Chemical analysis of samples of the cooked material indicated contents of sodium chloride ranging from about 4½ to 9%, of sodium nitrate from 1/20 to ½%, and of sodium nitrite from 15 to 55 parts per million. Each judge tasted samples from all 80 pieces in groups of four and at the rate of eight per day. Subjective appraisals of saltiness were expressed numerically in accordance with the convention currently adopted in these laboratories. In this, which

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[2] *Biometrician.*

differs from the one previously used (3), zero represents the ideal in the estimation of the judge, and excess or deficiency of the flavour in question is rated on an integral scale of + 5 to − 5.

Results

An analysis of the variance (2) of the 1840 foregoing individual assessments gave mean squares of 54.743 between judges (averaged over all samples), of 11.783 between pieces (averaged over all judges), and of 1.133 for the residual fluctuations of individual ratings. The standard deviation of an average rating appropriate to intra-panel comparisons of pieces was thus $\sqrt{1.133/23}$, i.e., $\pm\ 0.22$. To attain the 5% level of statistical significance therefore, a difference in the average ratings of two pieces would have to be at least $1.96\sqrt{2 \times 1.133/23}$, namely, $\pm\ 0.61$. To reduce this 'necessary difference' to $\pm\ 0.50$ would have required a panel of 35 judges.

From the mean squares listed in the preceding paragraph the underlying 'population variance' of judges' averages may be estimated (1) at $(54.743 - 1.133)/80$, corresponding to a standard deviation of $\pm\ 0.82$, although this figure, which involves one component based on only 22 degrees of freedom, is subject to correspondingly more uncertainty than that for the residual variance, for which 1738 degrees of freedom were available. From this estimate, therefore, it would have to be inferred that to be regarded as statistically significant at the 5% level, a difference in average ratings of samples assessed by two separate panels of the same size and variability as the one here considered would have to amount to at least $2.069\sqrt{2 \times (0.6701 + 1.133)/23}$ i.e., to $\pm\ 0.82$. Panels of the order of 60 members each would therefore be estimated as required to reduce this inter-panel necessary difference to $\pm\ 0.50$. If each judge made two independent assessments of samples from the same piece, this number would be reduced to rather more than 40, but only at the cost of increasing the total number of man-hours devoted to assessment in the ratio of about 85 to 60, as well as of entailing a corresponding increase in the quantity of test material and in the labour of preparation.

As in all the four cases previously considered, there were pronounced differences in personal preference, the average assessment of the saltiness of all 80 pieces by individual judges ranging from + 3.24 to − 0.54, i.e., from considerably over to slightly under the desired amount. The average assessment by the panel as a whole was + 1.20. Table I shows the deviation of the average for each judge from that of the remainder of the panel, and also lists the correlation and regression coefficients relating the assessment of single samples by each judge to the average assessment of samples of the same piece by the rest of the panel. As the average numerical assessment of the various pieces ranged only from + 2.70 to − 1.13, while the irregular fluctuation of single assessments has already been noted as giving rise to a mean square deviation of 1.133, generally high coefficients of correlation of individual with group assessments could not be expected. In fact the highest obtained was

TABLE I

STATISTICAL CHARACTERISTICS OF INDIVIDUAL JUDGES' ASSESSMENTS

Judge	Average deviation from mean of all others	Coefficient of correlation with means of all others	Coefficient of regression on means of all others
No. 1 (male)	− 0.08	.57***	0.85
No. 2 (female)	− 0.31	.59***	1.32
No. 3 (male)	− 0.53	.63***	0.78
No. 4 (male)	− 0.26	.45***	0.39
No. 5 (male)	+ 0.89	.57***	0.90
No. 6 (male)	+ 0.84	.69***	1.06
No. 7 (male)	+ 1.07	.33**	0.52
No. 8 (female)	− 0.38	.41***	0.69
No. 9 (male)	− 0.89	.11	0.02
No. 10 (female)	+ 0.20	.56***	0.89
No. 11 (male)	+ 0.97	.70***	1.72
No. 12 (female)	− 0.12	.64***	0.82
No. 13 (male)	− 0.33	.51***	0.55
No. 14 (female)	− 1 06	.47***	0.60
No. 15 (male)	+ 0.45	.64***	0.92
No. 16 (male)	− 0.02	.66***	1.52
No. 17 (female)	− 0.47	.46***	0.64
No. 18 (male)	+ 0.26	.62***	1.18
No. 19 (male)	+ 2.13	.43***	0.93
No. 20 (male)	− 0.17	.70***	1 18
No. 21 (male)	− 1.11	.15	0.37
No. 22 (male)	− 1.82	.32**	0.59
No. 23 (male)	+ 0.78	62***	1.24

** *Attains 1% level of statistical significance.*

*** *Attains 0.1% level of statistical significance.*

0.70. However, eight of the judges had coefficients in excess of 0.60, which in the circumstances are regarded as reasonably satisfactory, and those of only two were not statistically significant.

The range of individual sensitivity indicated by the regression coefficients of Table I is greater than that provided by the previously reported (3) assessments of over-all palatability. Judge No. 20, with an average deviation from the mean of all others of only − 0.17 unit, a correlation coefficient of 0.70, and a regression coefficient of 1.18, conformed most closely to the average reaction of the group as a whole. No. 11, who had an average deviation of + 0.97 and correlation and regression coefficients of 0.70 and 1.72 was the most sensitive to variations in saltiness, to which on the other hand Nos. 9 and 21 appeared to be very largely (the former almost completely) indifferent. Nos. 19 and 22, with average deviations from the mean of all other judges' assessments of + 2.13 and − 1.82, respectively, provided the individual extremes of aversion to and tolerance for saltiness. All the individuals specified were males, but the results as a whole were not indicative of any statistically significant average difference between the sexes in respect of either tolerance or sensitivity.

The present results differ from the majority of organoleptic assessments in that they may be appropriately related to specific chemical constituents of the cooked meat, and in this way it was found that the coëfficients of partial correlation of the average assessment and the sodium chloride and nitrate contents reported for the various pieces were + 0.62 and 0.25, respectively, the latter attaining the 5% level of statistical significance. The small variations in sodium nitrite recorded were without demonstrable effect on the assessment. It would be unjust to attribute the moderate level of even the first of these correlation coefficients entirely to inconsistency of the judges or masking effects of other flavours, as it was evident that the chemical determinations were themselves subject to appreciable sampling discrepancies.

The average assessment for each piece obtained from the panel as a whole was related to sodium chloride and nitrate content by the regression equation of least squares:

$$\begin{aligned} Assessment = &- 1.78 + 0.375\ (NaCl\ per\ cent) \\ &+ 0.090\ (NaNO_3\ per\ mille) \pm 0.45. \end{aligned}$$

As no significant reduction of the residual variance resulted from inclusion of the quadratic term in NaCl, it was inferred that the relation was sensibly linear over the range considered.

Owing to its rather limited range of saltiness, the present series of observations is not very informative in respect of the variance of individual assessments at different average preference levels. The inter-judge standard deviations for all samples receiving average assessments between 0 and 1, between 1 and 2 and between 2 and 3 were ± 1.29, ± 1.18, and ± 1.43, respectively. The last of these is significantly larger than either of the other two, and thus provides some indication of slightly greater divergence in the assessment of moderately unpalatable samples. Additional data are, however, required to investigate this point adequately.

Conclusions

These results for the specific attribute of saltiness of bacon are in qualitative agreement in four respects with those already reported (3) for general palatability of certain other foodstuffs. First, they indicate that single assessments by unselected judges were characterized by considerable random variation but also by a demonstrable element of correlation, making possible reproducible differentiation between samples by a panel of adequate size. Second, they again provide evidence of persistent differences in the preference level of individuals, necessitating substantially more judges for a specified degree of reproducibility in inter- than in intra-panel comparisons. Third, individual judges again exhibited a wide range of sensitivity as well as of tolerance. Fourth, there was some further indication of greater diversity in individual assessments of moderately unpalatable samples.

The significant degree of correlation of the panel assessments with the sodium chloride and nitrate content of the test material is a satisfactory feature of the present findings. From the regression equation given in the preceding section it may be computed that the degree of saltiness to the taste preferred by this panel would be obtained from a sodium chloride content of about 4¾% by weight of the cooked bacon in the absence of sodium nitrate, and of roughly 4% when 2½ parts per thousand of sodium nitrate was also present.

Acknowledgments

The data reported upon were recorded in the course of studies by Dr. N. E. Gibbons and Mr. G. A. Grant of the Food Investigations Group of these laboratories. Mr. F. L. Smith assisted largely in the statistical computations.

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FLAVOUR REVERSION IN HYDROGENATED LINSEED OIL

III. THE RELATION OF ISO-LINOLEIC ACID TO FLAVOUR DETERIORATION[1]

By H. W. Lemon[2]

Abstract

Further evidence that iso-linoleic acid is related to the unpleasant odour development when partially hydrogenated linseed oil is heated is as follows:

(*a*) Partially hydrogenated perilla oil, containing considerable iso-linoleic acid, developed the same odour when heated, as did partially hydrogenated linseed oil.

(*b*) A concentrate of iso-linoleic acid developed a similar odour when it was heated. Distillation of the acid, or removal of unsaponifiable substances, had no effect on the odour development.

(*c*) When fatty acid fractions obtained by crystallization of the acids from hydrogenated linseed oil were re-esterified with glycerol, and subjected to the heat test, most odour development occurred in the fraction containing most iso-linoleic acid.

Increasing the selectivity of hydrogenation did not greatly affect the formation or hydrogenation of iso-linoleic acid. However, products of high temperature (200° to 250° C.) hydrogenations were softer for equivalent iodine numbers, and had lower melting points than those from low temperature hydrogenations.

Hydrogenation of partly polymerized linseed oil yielded a product that when heated did not develop the characteristic odour of hydrogenated linseed oil.

It was reported in a previous publication (8) that when linseed oil is hydrogenated an isomeric linoleic acid is formed in which the double bonds are in such positions that they will not form a conjugated system upon alkali isomerization. Some experimental evidence was presented that indicated that the isomeric acid may be responsible for the characteristic odour that develops when partially hydrogenated linseed oil is heated to baking and frying temperatures. It was suggested that hydrogenation of linseed oil should be highly selective in order that the iso-linoleic acid may be completely hydrogenated without the formation of large quantities of saturated acids.

In the present paper further evidence that iso-linoleic acid plays a part in flavour development on heating is presented, together with the results of experiments to reduce its amount in the product: (*a*) by increasing the selectivity of hydrogenation and (*b*) by reducing the linolenic acid content of linseed oil by polymerization

Methods

Analytical methods and the techniques used for refining, bleaching, hydrogenation, and deodorizing have been described (8). Linolenic and linoleic acids were determined by the spectral method of Mitchell, Kraybill, and

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[2] *Research Fellow.*

Zscheile (10) as modified by Brice, Swain, Schaeffer, and Ault (6). Saturated and iso-oleic acids were determined by the method of Baughman and Jamieson (4).

Polymerization of linseed oil was done in a 2 litre three-necked flask equipped with thermometer, a tube for bubbling carbon dioxide through the oil, and a goose neck leading to a condenser. The reaction was carried on under vacuum at 315° C.

Experimental and Results

A. Relation of Iso-linoleic Acid to Odour Development

Hydrogenation of Perilla and Tung Oils

The amount of linolenic acid in perilla oil is as much as, or more than, that in linseed oil, and so perilla oil might be expected to yield a hydrogenation product similar in respect to flavour reversion characteristics to that produced by linseed oil. Tung oil contains a large proportion of eleostearic acid, an isomer of linolenic acid, and it is unlikely that its hydrogenation would produce the same iso-linoleic acid as hydrogenation of linolenic acid. Therefore, a quantity of each of these oils was hydrogenated to a plastic consistency, and samples subjected to the heat test.

The perilla oil was alkali-refined, hydrogenated, and deodorized in the usual manner. Samples were taken for fatty acid analysis, and the results are given in Fig. 1. As in the case of linseed oil, iso-linoleic acid was produced on hydrogenation. The tung oil was hydrogenated without refining. Samples were examined for diene and triene conjugation before and after alkali isomerization with the use of a Beckman spectrophotometer; the absorption curves are shown in Fig. 2. Saturated and iso-oleic acids were not determined. There was a decrease in triene conjugation on hydrogenation but very little development of diene conjugation. Alkali isomerization had little effect on the amount of diene and triene conjugation present. These results indicate that, when eleostearic acid is hydrogenated under the conditions described, two or more double bonds are saturated simultaneously.

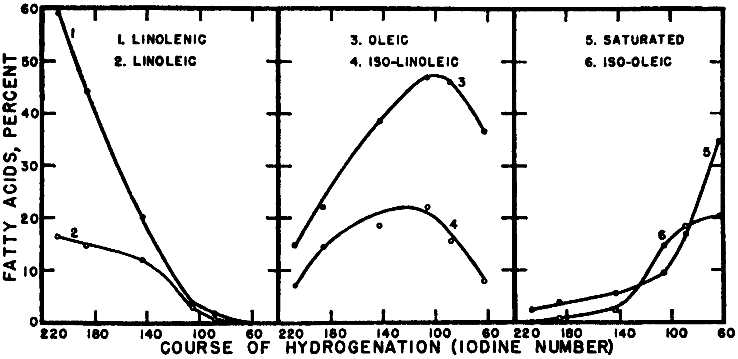

FIG. 1. *Progressive change in fatty acid composition on hydrogenation of perilla oil.*

The hydrogenated perilla, linseed, and tung oils, and a standard all-hydrogenated shortening were heated to 200° C. The hydrogenated perilla and hydrogenated linseed oils developed the same unpleasant odour, the two being indistinguishable. The hydrogenated tung oil, with an apparent iodine number of 58.6, did not develop such an odour. This experiment provided further evidence that the substance responsible for the unpleasant odour of hydrogenated linseed oil is formed by the hydrogenation of linolenic acid.

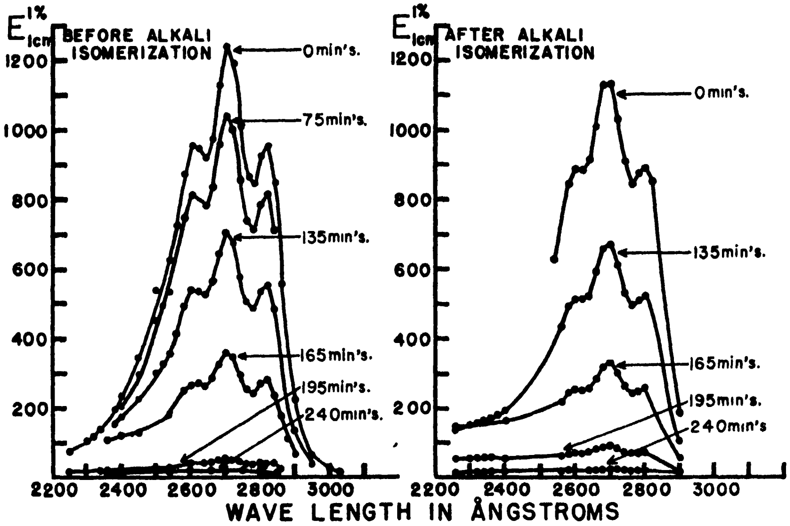

FIG. 2. *Effect of hydrogenation time on ultraviolet absorption by tung oil.*

Heat Tests on Iso-linoleic Acid

It was stated in the first paper of this series (8) that a strong odour resembling that of heated hydrogenated linseed oil developed on heating a distilled iso-linoleic acid concentrate. The odour was quite different from that of linolenic, linoleic, or oleic acids treated in the same way.

It was thought that the odour might be caused by some unsaponifiable substance associated with the iso-linoleic acid. Therefore a quantity of the acid in alcoholic solution was neutralized with potassium hydroxide, diluted with water, and the soap solution extracted several times with ether. The acids were liberated from the soap, washed with water, dried, and distilled from a Hickman alembic flask. On heating, the acids developed the same strong odour, resembling that of hydrogenated linseed oil.

Fractional Crystallization of Fatty Acids from Hydrogenated Linseed Oil

The isolation of a concentrate of iso-linoleic acid by low temperature crystallization of the separated fatty acids of hydrogenated linseed oil was described in the first paper of this series (8). In a similar separation, four fatty acid fractions were obtained. The first of these consisted of the acids that precipitated from acetone at −30° C.; the second fraction precipitated at from −30° to −60° C. The third fraction consisted of all of the crystalline precipitates that could be obtained by chilling to −60° C. the concentrated filtrate from the previous precipitations, and the fourth fraction, consisting largely of iso-linoleic acid, was obtained from the final filtrate.

Each of these fractions was esterified with glycerol in the proper amount to yield triglyceride. The products were deodorized. The fat made from the first fraction was quite hard, that from the second fraction was semisolid, and those from the third and fourth fractions were liquid at room temperature.

The four fats were heated to 200° C. There was little, if any, development of the reverted odour in the first fat but the fourth fat developed a very strong odour. Numbers two and three were similar, and intermediate to numbers one and four. There was no doubt that the odour development was caused by heating the iso-linoleic glyceride itself, or some substance associated with it.

B. INFLUENCE OF SELECTIVITY ON HYDROGENATION OF ISO-LINOLEIC ACID

It was felt that hydrogenated linseed oil would be more suitable for use as a shortening if the iso-linoleic acid content were reduced or eliminated, and it was thought that some improvement might be made by increasing the selectivity of hydrogenation. It has been pointed out by Bailey, Feuge, and Smith (2) that selectivity is increased by raising the temperature or catalyst concentration, and by decreasing the pressure or agitation, and that each of the conditions contributing to selectivity causes a greater formation of iso-oleic acid.

Three series of hydrogenations were completed. In the first series the temperature was kept low during the initial period of the hydrogenations but was raised rapidly when the refractive index (Zeiss butyro) had dropped to about 58 at 40° C. corresponding to an iodine number of approximately 120; at the same time the gauge pressure was reduced from 25 to 5 lb. It was hoped that increasing the temperature at about iodine number 120 would suppress the rapid formation of saturated acids which normally begins at about this point, and at the same time favour the hydrogenation of iso-linoleic acid. Various temperature combinations were tried. In the second and third series of hydrogenations, four temperatures between 120° and 250° C. were selected, and the oil and catalyst mixtures were brought to these temperatures as rapidly as possible. A slight positive pressure of hydrogen was maintained during the period required to bring the oil to the desired temperature; it was then increased to 25 lb. gauge pressure.

In all three series, samples were taken at intervals during the hydrogenations for fatty acid analysis. The results are given in Table I. By plotting these results against iodine number, saturated and iso-linoleic acid values at iodine number 90 were determined for the low to high temperature series. These values are given in Table II. It is apparent that raising the temperature of hydrogenation at iodine number 120 had no appreciable effect on the subsequent hydrogenation of iso-linoleic acid.

TABLE I

Analysis of hydrogenated linseed oil samples

Hydrogenation temperature, ° C.	Time, min.	Iodine number	Fatty acid composition, %					
			Saturated	Iso-oleic	Oleic	Iso-linoleic	Linoleic	Linolenic
Series I. Low to high temperature hydrogenations								
140	20	148.5	7.4	1.9	40.8	5.6	15.2	29.1
140	40	120.8	10.1	4.0	48.1	14.9	10.9	12.0
140	60	94.4	17.0	7.5	50.9	17.1	5.4	2.1
140	70	79.6	23.1	10.7	50.1	13.8	1.8	0.5
115-190	30	163.2	6.5	0.9	36.0	1.5	17.0	38.1
115-190	75	119.6	10.9	3.4	46.9	16.8	11.5	10.5
115-190	100	97.8	13.6	9.0	51.7	20.5	3.9	1.3
115-190	115	79.2	21.5	19.0	45.9	13.5	0.1	0
115-240	45	147.0	7.4	1.5	40.1	8.2	16.6	26.2
115-240	80	112.4	11.9	3.9	48.6	18.7	10.2	6.7
115-240	95	89.0	15.0	15.4	51.4	16.6	1.2	0.4
115-240	100	82.8	17.1	22.8	46.6	13.4	0.1	0
140-190	20	152.3	8.2	2.3	36.3	5.1	17.1	31.0
140-190	50	108.1	12.2	6.9	48.3	19.4	8.2	5.0
140-190	60	96.4	14.3	12.1	49.0	18.9	4.1	1.6
140-190	75	81.9	17.7	16.7	52.7	12.7	0.2	0
140-235	25	146.0	7.9	2.1	39.6	7.8	16.4	26.2
140-235	45	106.7	12.1	5.5	51.6	17.4	8.2	5.2
140-235	55	84.3	18.2	16.4	50.3	12.9	1.2	1.0
140-235	60	72.0	23.0	28.8	41.0	6.4	0.5	0
Series II. Effect of temperature of hydrogenation on selectivity								
120	60	132.5	10.0	2.8	40.3	18.3	12.4	16.2
120	90	106.4	14.6	6.0	46.4	20.4	7.7	4.9
120	120	88.1	20.9	8.3	49.0	16.6	3.8	1.4
120	155	70.5	31.2	10.0	46.0	11.6	1.0	0
150	30	128.0	10.3	3.3	42.1	18.2	12.2	13.9
150	45	103.7	15.2	6.3	47.3	20.4	6.5	4.3
150	60	80.3	25.3	9.7	48.8	15.2	1.0	0.8
150	80	53.9	43.7	10.8	39.2	6.1	0.2	0
200	25	93.5	14.6	14.3	49.3	18.1	2.3	1.4
200	30	80.1	20.4	15.9	50.7	12.0	0.6	0.4
200	40	59.9	36.4	17.9	39.7	5.7	0.3	0
200	45	47.8	47.7	14.3	34.7	3.2	0.1	0
250	20	95.6	12.0	17.6	48.7	17.5	2.9	1.3
250	25	80.9	18.8	23.4	45.0	12.2	0.6	0
250	30	67.5	26.8	27.6	40.3	5.1	0.2	0
250	35	56.8	37.6	20.4	38.3	3.6	0.1	0

TABLE I—*Continued*

ANALYSIS OF HYDROGENATED LINSEED OIL SAMPLES—*Continued*

Hydrogenation temperature, ° C.	Time, min.	Iodine number	Fatty acid composition, %					
			Saturated	Iso-oleic	Oleic	Iso-linoleic	Linoleic	Linolenic
Series III. Effect of temperature of hydrogenation on selectivity								
120	60	146.0	9.7	2.5	32.6	18.1	13.8	23.3
120	120	105.6	16.4	8.5	40.2	21.4	6.5	6.0
120	160	80.4	27.2	11.3	42.0	16.1	2.3	1.1
120	170	72.8	30,9	10.3	44.0	12.9	1.1	0.8
120	190	58.7	39.7	9.5	42.7	7.5	0.6	0
150	25	135.4	9.3	4.3	38.9	17.0	12.2	18.3
150	50	103.7	12.6	12.2	46.6	18.9	5.4	4.3
150	65	83.9	19.7	17.0	46.0	16.2	1.1	0
150	75	75.0	25.7	17.3	42.1	13.4	0.5	0
150	95	49.8	45.9	16.5	33.6	4.0	0	0
200	25	116.6	8.6	12.0	45.4	15.4	9.0	9.6
200	33	93.8	10.9	26.0	43.7	18,1	0.8	0.5
200	42	82.2	16.5	32.9	39.5	11.1	0	0
200	51	67.8	27.1	30.7	36.2	6.0	0	0
200	55	62.0	31.8	27.9	36.1	4.2	0	0
240	20	115.8	9.6	11.8	43.2	18.7	8.4	8.3
240	24	103.1	10.3	18.4	43.6	21.1	4.4	2.2
240	33	90.7	13.6	22.6	44.8	17.8	1.2	0
240	45	78.0	19.3	23.4	47.4	9.5	0.35	0
240	65	65.7	27.8	23.6	43.3	5.3	0	0

TABLE II

EFFECT OF RAISING THE TEMPERATURE DURING HYDROGENATION ON THE CONTENT OF SATURATED AND ISO-LINOLEIC ACIDS AT IODINE NUMBER 90

Hydrogenation temperature, ° C.	Saturated acids, %	Iso-linoleic acid, %
140	19.0	16.5
115-190	16.5	18.5
115-240	15.0	16.5
140-190	15.5	17.5
140-235	16.0	15.0

In Fig. 3 the effect of temperature of hydrogenation on fatty acid composition at iodine numbers 80 and 90 is shown for Series II hydrogenations. Increasing the temperature caused more complete hydrogenation of linolenic and linoleic acids, increased formation of iso-oleic acid, and decreased production of saturated acids; however, it had little effect on the hydrogenation of iso-linoleic and oleic acids. These conclusions are in agreement with those of Bailey and Fisher (3), who found that iso-linoleic acid is much more resistant to hydrogenation than linoleic or linolenic acids.

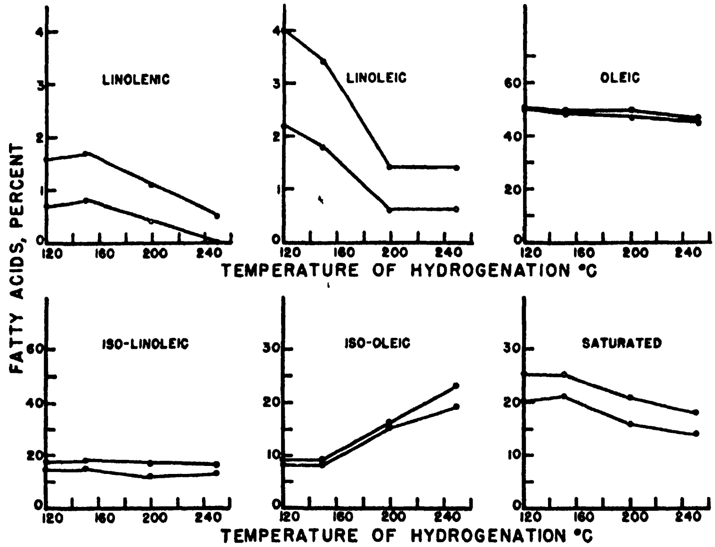

FIG. 3. *Effect of temperature of hydrogenation on the fatty acid composition of hydrogenated linseed oil.*

The melting points of samples from Series III hydrogenations were determined by the capillary tube method, and their micropenetration values at 25° C. were determined with a micropenetrometer similar to that described by Feuge and Bailey (7). The values obtained have been plotted against iodine numbers (Fig. 4). It is evident that the melting points of samples taken from the high temperature hydrogenations were lower for equivalent iodine numbers than those of samples taken from the low temperature hydrogenations. Similarly, the penetration values at 25° C. of samples from the high temperature hydrogenations were greater than those of samples of the low temperature hydrogenations for equivalent iodine numbers, although the difference became less as hydrogenation proceeded.

From the results, the iodine number corresponding to a melting point of 47° C. has been estimated for hydrogenations done at 250°, 200°, 150°, and 120° C., respectively, and the fatty acid composition for each of these iodine numbers has been determined from the results in Table I. These values are given in Table III.

It can be concluded that if linseed oil is hydrogenated at a high temperature, it can be saturated to a lower iodine number without becoming too hard, giving a product with a lower iso-linoleic acid content. However, when samples having a lower iso-linoleic acid content were heated, there was still a strong odour development, and it was difficult to determine whether there was any improvement.

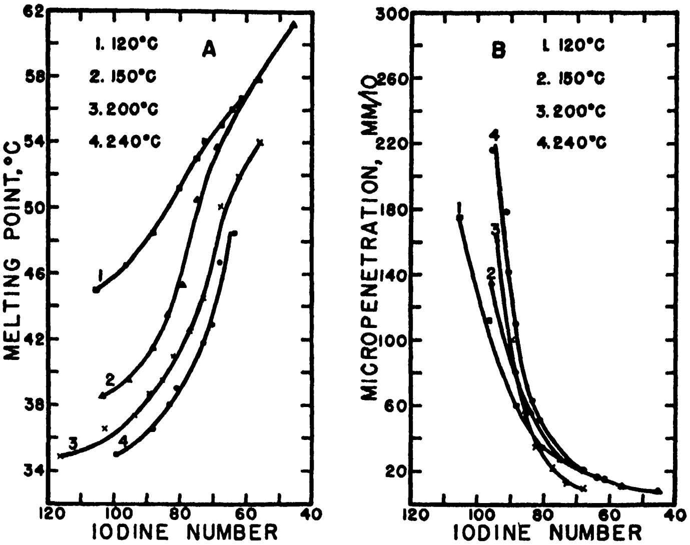

FIG. 4. *Effect of temperature of hydrogenation of linseed oil on melting point (Graph A) and on micropenetration at 25° C. (Graph B).*

TABLE III

EFFECT OF TEMPERATURE OF HYDROGENATION OF LINSEED OIL ON THE FATTY ACID COMPOSITION AT MELTING POINT OF 47° C.

Hydrogenation temperature, ° C.	Iodine number	Fatty acid composition, %					
		Saturated	Iso-oleic	Oleic	Iso-linoleic	Linoleic	Linolenic
120	94	21.2	10.3	41.7	19.2	4.4	3.3
150	79	22.5	17.2	44.5	14.5	0.7	0
200	70	25.0	31.4	37.0	6.5	0	0
240	66	27.5	23.6	43.5	5.5	0	0

C. HYDROGENATION OF POLYMERIZED LINSEED OIL

When linseed oil is polymerized, there is a reduction in the linolenic and linoleic acids content. There is a commercial process in operation that entails polymerization followed by extraction of the non-polymerized portion with acetone (5). As this results in an oil with a low concentration of linolenic acid it has been suggested that the oil might be used as an edible oil. Privett, Pringle, and McFarlane (11) have developed a similar process, involving milder polymerization, for the purpose of obtaining an edible fraction from linseed oil. In view of this work it was decided to determine quantitatively by the spectral method the disappearance of linolenic and linoleic acids on polymerization, and to hydrogenate oils polymerized to varying degrees and apply heating tests in order to determine their susceptibility to reversion.

Polymerization was carried on for 20 min., one hour, two hours, and three hours. Refractive index, free fatty acid, and linolenic and linoleic acids were determined for each product. The results are given in Table IV. It is evident that, although the disappearance of linolenic acid on polymerization is rapid, there is still some present after heating for three hours.

TABLE IV

POLYMERIZATION OF LINSEED OIL

Time of polymerization	Refractive index, 50° C.	Free fatty acid, % as oleic	Linoleic acid, %	Linolenic acid, %
0 min	1.4699	0.05	19.6	51.9
20 min.	1.4715	1.2	14.4	43.1
1 hr.	1.4744	1.8	13.9	26.6
2 hr.	1.4771	2.8	11.2	13.9
3 hr.	1.4790	3.7	9.1	7.5

Each of the polymerized oils was hydrogenated without any further treatment. The hydrogenations proceeded with some difficulty, probably owing to the high free fatty acid content. The products were deodorized, and samples heated to 200° C. on a hot plate. The hydrogenated linseed odour was present in the product from the 20 min. polymerization, but there was little, if any, of it in the others.

Discussion

There is considerable evidence that the unpleasant flavour and odour of heated hydrogenated linseed oil are caused by the decomposition of iso-linoleic acid, although there is some indication from storage tests (9) that this is not the only cause of flavour deterioration. Reversion in unhydrogenated oils, such as soybean, is not explained by the iso-linoleic acid theory, and it is probable, as has been suggested by Bailey (1), that in this case it is the result of a different mechanism.

If iso-linoleic acid plays a part in reversion its removal from hydrogenated linseed oil presents a difficult problem. The results of the experiments to determine the effect of selectivity on its hydrogenation were not encouraging, as it apparently hydrogenates with difficulty, and quantities of it persist until the product has become very hard regardless of the conditions of hydrogenation.

Acknowledgments

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FLAVOUR REVERSION IN HYDROGENATED LINSEED OIL

IV. FURTHER PROCESSING STUDIES[1]

By H. J. Lips[2]*, H. W. Lemon[3], and G. A. Grant[4]

Abstract

Flavour reversion could not be detected in samples of hydrogenated linseed oil stored under vacuum in the dark. In samples exposed to the air, reversion occurred without appreciable increase in peroxide oxygen or Kreis values, particularly in products of low iodine number, while accompanying changes in fluorescence were slight and erratic. An observed 'bad area' for susceptibility in the lower iodine number range suggests that iso-linoleic acid (4) is not the only cause of reversion. No improvement in flavour stability was obtained by: low to high temperature hydrogenation (110° to 240° C. (230° to 464° F.)), removal of impurities from the oil, or the use of a linseed oil fraction from a commercial polymerization process.

A previous paper in this series (6) dealt with storage studies to determine the effect of various modifications in processing procedure upon the susceptibility of hydrogenated linseed oil to flavour reversion. The present investigation is an extension of that work.

Experimental

Standard processing techniques, the method of estimating storage life by flavour scores, and some of the chemical measurements used have been described (4, 6). In this study some of the samples were stored at 60° C., rather than at 43.3° C., to obtain comparative results in a shorter time. As earlier work demonstrated that any chemical changes accompanying flavour reversion would be difficult to detect, sensitive modifications of the peroxide oxygen (7) and Kreis (12, 13) tests were introduced as estimates of oxidative deterioration. To investigate possible changes in fluorescence, readings of xylol solutions of the fat were made in a Coleman photofluorometer (3).

Vacuum Storage

It has not been clearly established that the presence of oxygen is essential for flavour reversion (10). To examine the effects of oxygen-free storage on hydrogenated linseed oil, melted samples were evacuated in glass tubes on a high vacuum apparatus for four hours, and sealed off at a pressure of 5μ. These tubes were stored in the dark at 43.3° C. together with an untreated control sample of the same shortening.

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* *Earlier publications by this author appeared under the name A. Lips.*

The control sample developed definite flavour reversion in 11 weeks while the vacuum-stored material had no detectable reverted odour at the end of 60 weeks' storage. The control had a peroxide value of 2.4 ml. of 0.002 *N* thiosulphate per gm. (iodimetric method) at the end of 11 weeks. At 60 weeks the peroxide value of the vacuum-stored material was nil, even by the more sensitive ferrometric procedure.

Removal of Impurities

A number of attempts have been made to account for flavour reversion on the basis of impurities in oils. Voskresenkii and Dobruinina (11), working on soybean oil, reported an odorous constituent that had a variable nitrogen content and reduced Fehling's solution. Marcelet (8) isolated from vegetable oils saturated and unsaturated hydrocarbons having nauseous odours, and Bickford (2) isolated similarly objectionable material from the condensate obtained from a commercial soybean oil deodorizer.

Removal of possible sources of flavour instability in linseed shortening was attempted by deodorizing and by winterizing refined and bleached linseed oil, before hydrogenating and deodorizing in the usual manner. Table I shows the negative results. Preliminary deodorization at 270° C. was strongly detrimental, as evidenced by a short storage life and a high mean peroxide value.

Low to High Temperature Hydrogenation

Previous investigations on the effect of different conditions of hydrogenation upon flavour stability were continued. A selective hardening of linseed oil is desirable because of the high proportion of linolenic acid that must be hydrogenated. It is also important that the formation of iso-linoleic acid be minimized, since the breakdown of this compound is considered to be a cause of flavour reversion (4).

A hydrogenation procedure in which the temperature was raised during the process from a low to a high value appeared to offer a means of hydrogenating iso-linoleic acid without building up a high concentration of saturated acids (5). A series of samples of linseed shortening was prepared in the manner previously described, employing temperatures in the range 110° to 240° C., and available commercial- and laboratory-prepared nickel catalysts (4, 6). Temperature ranges, catalysts, peroxide values (iodimetric method) averaged over the entire sampling period (56 weeks), and storage lives are given in Table I. Storage tests at 43.3° C. showed no improvement in the products obtained over the average for standard processing. Mean peroxide values were low, except in the case of one of the 110° to 160° C. samples, indicating the usual resistance to oxidation.

Hydrogenation to Various Iodine Numbers

Earlier work reported susceptibility to flavour reversion at a maximum at iodine value 80 to 130, with complete stability at iodine value 6 (4, 6). It was assumed that susceptibility varied with the amount of iso-linoleic acid present.

TABLE I

STORAGE LIFE AND MEAN PEROXIDE VALUE OF LINSEED SHORTENINGS PREPARED BY VARIOUS PROCESSING PROCEDURES AND STORED AT 43.3° C. FOR 56 WEEKS

Group	Group variant			Storage life, weeks	Mean peroxide value*, ml. per gm.
	Alkali treatment, ° Bé	Catalyst	Temperature range, ° C.		
Low to high temperature hydrogenation	30	Standard	110–160	18	8.1
	30	Standard	110–160	29	3.7
	30	Standard	110–190	17	1.0
	30	Standard	110–190	17	3.5
	30	Standard	115–190	17	3.1
	30	Standard	115–240	19	1.0
	30	Standard	140–190	15	1.3
	30	Standard	140–235	16	0.8
	30	Commercial	110–160	25	2.5
	30	Commercial	110–190	31	1.6
	30	Commercial	110–160	17	4.4
	30	Commercial	110–190	32	2.0
	40	Standard	115–190	15	1.2
	40	Standard	115–190	6	1.3
Additional deodorization	Deodorized at 200° C. before hydrogenation			16	9.6
	Deodorized at 270° C. before hydrogenation			1	31.6
Use of winterized oil	Winterized at 0° C. after refining			18	2.6
Average for 18 samples by standard procedure				29	
Estimated necessary difference				12	

* *Iodimetric method (13).*

However, it has since been noticed that flavour reversion is often pronounced at iodine values considerably lower than those that would be expected from the theory that iso-linoleic acid is the cause of reversion. This phenomenon was investigated further.

Two hydrogenations were carried out according to the usual processing technique in a large converter, so equipped as to permit removal of samples of varying degrees of saturation while the operation continued. Samples thus obtained were deodorized, stored at 60° C., and sampled at weekly intervals for nine weeks. Composition data for the two series are shown in Table II, and storage lives and mean values for peroxide oxygen (ferrometric method), Kreis test, and fluorescence are presented in Table III (*A*).

It will be seen that for both series of hydrogenated oils there was no regular improvement in storage life with decreasing iso-linoleic acid concentration. There was in fact an apparent slump in flavour stability at lower iodine values, contrary to previous observations based on a rapid heat test (6). It will also be noted that storage lives in the two series were not the same for similar

TABLE II

COMPOSITION OF SAMPLES OF HYDROGENATED LINSEED OIL OF DIFFERENT IODINE NUMBERS

Time of hydrogenation, min.	Iodine number	Fat acid content*, %					
		Saturated	Iso-oleic	Oleic	Iso-linoleic	Linoleic	Linolenic
Series 1							
33	88.3	20.9	10.4	47.6	15.4	3.5	2.2
38	77.3	27.1	12.9	44.2	13.0	1.8	1.0
45	60.8	38.7	13.1	38.9	8.5	0.8	0
49	52.8	44.3	12.2	37.8	5.3	0.4	0
53	40.2	55.6	8.2	33.8	2.0	0.4	0
58	39.9	—	—	—	—	0.3	0
Series 2							
35	89.4	20.6	10.3	49.0	15.1	3.8	2.2
42	77.6	26.7	11.3	45.8	13.7	1.8	0.7
50	62.2	37.4	12.7	40.0	9.2	0.7	0
54	53.6	44.0	12.1	37.6	5.9	0.4	0
58	48.2	47.4	8.8	40.3	3.2	0.3	0
62	42.2	53.2	8.0	36.4	2.0	0.3	0

**For method of determination see Ref. (4).*

TABLE III

MEAN PEROXIDE, KREIS AND FLUORESCENCE VALUES, AND STORAGE LIVES, FOR LINSEED SHORTENINGS STORED AT 60° C. FOR NINE WEEKS

Group	Group variant	Mean values of measurements on stored samples			Storage life[3], weeks
		Peroxide oxygen content*, m.e. per kgm.	Kreis value, extinction coefficients	Fluorescence, photo-fluorometer units	
A. Varying iodine number	Series 1				
	88.3	53.9	44.2	72.0	2.4
	77.3	22.8	22.0	74.0	2.2
	60.8	9.7	9.0	64.5	3.6
	52.8	9.7	8.3	60.7	2.8
	40.2	6.7	5.7	61.7	3.2
	39.9	4.5	5.9	58.4	4+
	Series 2				
	89.4	42.2	36.1	70.3	1.8
	77.6	24.3	20.5	68.6	1.8
	62.2	9.2	9.2	63.6	3.9
	53.6	8.3	7.2	60.2	3.6
	48.2	6.8	6.3	56.7	3.0
	42.2	5.9	4.8	56.2	5+
B. Commercial polymerized oil fraction	Hydrogenated	14.9	22.4	48.9[1]	0.7
	Hydrogenated	30.9	27.5	39.8[1]	0.5
	Esterified and hydrogenated	70.5	23.4	56.5[2]	1.8

* *Ferrometric method (7).*

[1] *1 : 50 dilution.*

[2] *1 : 100 dilution. All other fluorescence measurements 1 : 10 dilution.*

[3] *Estimated necessary difference: one week.*

iodine values. This may have been due to different rates of hydrogenation, since the composition data do not indicate any reason for the discrepancies.

At the higher iodine values there was some increase in Kreis and peroxide values before the appearance of definite flavour reversion. This increase was steady with no definite changes in the rate of accumulation and appeared to be independent of reversion. Below iodine number 60 these values remained practically stationary. Fluorescence showed a decrease during storage but the changes were erratic throughout. Fluorescence values were generally higher at the higher iodine numbers.

Use of Polymerized Oils

In view of the stability to reversion found in hydrogenated, acetone-segregated fractions of polymerized linseed oil (9), a commercial product (1) obtained by solvent extraction of polymerized linseed oil was examined. In addition to the regular polymerized fraction, two laboratory-prepared materials (5) were hydrogenated.

The commercial process of acetone extraction of polymerized linseed oil yields an oil that is very dark in colour, and has a 'strong bodied oil' odour. The free fatty acid content is high, about 13% expressed as oleic acid, and this cannot be removed by ordinary refining methods, since emulsifying properties prevent the 'break'. Alkali refining has been found unsuccessful even after lengthy steam deodorization, so the regular commercial fraction was esterified with glycerol to reduce the free fatty acid content to 1.6%. Refractive index, linoleic acid, linolenic acid, and free acid content for all three samples are shown in Table IV. The linoleic and linolenic acid contents of the laboratory-prepared fractions were high since these were obtained from only partially polymerized oils. However, even in the regular product the content of these acids was still appreciable.

TABLE IV

ANALYSIS OF SOLVENT SEGREGATED FRACTIONS OF POLYMERIZED LINSEED OIL

Sample	Refractive index at 50° C.	Linoleic acid, %	Linolenic acid, %	Free fatty acid as oleic, %
Laboratory sample	1.4736	14.4	33.0	2.1
Laboratory sample	1.4729	11.5	22.3	3.6
Regular process sample, esterified with glycerol	1.4750	9.3	8.3	1.6

The three samples were hydrogenated with difficulty (5). There was considerable foaming of the oils, and on deodorizing a large amount of crystalline material (acid number 126.5) tended to choke the side-arm of the deodorizing flask. The final products were dark coloured. Owing to the presence of polymerized acids in the products, saturated acids could not be estimated by the usual method and hence the amount of iso-linoleic acid could not be determined.

The products were stored at 60° C. as outlined in the preceding section. Storage lives and mean values for the chemical tests are shown in Table III (*B*). Storage lives were short, although there was some doubt among members of the testing panel that the off-odours developed were typical reverted odours of hydrogenated linseed oil. As indicated by the high mean values for peroxide and Kreis tests these products were unstable to oxidation. Mean fluorescence was much higher than with ordinary linseed shortening.

Discussion

The experiments outlined indicate no solution to the flavour reversion problem by removal of impurities from the oil, by selective hydrogenation, or by the use of solvent-segregated material from a commercial polymerization process.

The failure of selective hydrogenation to minimize reversion may be explained in part by the finding that iso-linoleic acid is more resistant to hydrogenation than linoleic or linolenic acids (5). The use of commercial fractions of polymerized oils does not appear promising, because of their high colour and free fatty acid, and emulsifying properties. Moreover, the polymerization does not alter all the linolenic acid, and the hydrogenated products are unstable to oxidation and contain polymerized material of undetermined nature. However, it must be emphasized that the commercial process is not identical with the procedure reported by Privett, Pringle, and McFarlane (9), which yields a more acceptable product.

The storage experiments with shortenings of various iodine values suggest that iso-linoleic acid is not the only cause of reversion. They also confirm earlier views that flavour changes may occur without appreciable oxidative changes, although the vacuum storage results are evidence that some oxygen must be present for reversion to take place.

Acknowledgments

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RATION BISCUITS

IV. EFFECT OF TEMPERATURE AND SHORTENING TYPE ON KEEPING QUALITY[1]

By H. J. Lips[2*], N. C. Crowson[3], and W. Harold White[4]

Abstract

Biscuits commercially prepared with shortenings of four types (compound animal–vegetable, blended vegetable, hydrogenated vegetable, and stabilized, hydrogenated vegetable) were coarsely ground and stored in sealed cans at 26.7°, 43.3°, and 60° C. (80°, 110°, and 140° F.). Deterioration was assessed by peroxide oxygen and pH determinations, and by flavour scores. The results obtained for biscuits stored at 60° C. were not indicative of behaviour at the lower temperatures. Flavour score was the most useful estimate of biscuit keeping quality, especially at 26.7° and 43.3° C. Peroxide development was appreciable only in biscuit material stored at 26.7° C.

Biscuits prepared with hydrogenated vegetable shortenings were generally more stable (average storage life: 84, 22, and 13 weeks at 26.7°, 43.3°, and 60° C., respectively) than those prepared with animal–vegetable or blended vegetable shortenings. However, shortenings with Swift stabilities (110° C.) greater than 40 hr. did not yield products of increased keeping quality.

Introduction

One of the important causes of spoilage in baked goods is deterioration of the fat used in their preparation. Therefore it might be expected that the keeping quality of a baked product would bear a direct relation to the keeping quality of the shortening used. However, determination of shortening stability does not necessarily indicate the stability that the shortening will show in soda crackers (4, 12, 13). This has been attributed in part to destruction of antioxidants and peroxides in the fat during baking.

A previous investigation in these laboratories demonstrated that ration biscuits had a longer storage life at 43.3° C. when a stabilized, hydrogenated vegetable, rather than a compound, animal–vegetable shortening was used (5). The present paper describes an examination of a number of biscuit shortenings and the results obtained from storage tests on ration biscuits prepared with these shortenings.

Materials and Methods

Seventeen currently available shortenings (1943) were classified according to information received from the manufacturers into four general groups: I,

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* *Earlier publications by this author appeared under the name A. Lips.*

compound animal–vegetable; II, blended all vegetable; III, hydrogenated vegetable; and IV, stabilized, hydrogenated vegetable. Keeping quality was estimated by Swift stability tests at 110° C. (9) and by peroxide measurements (15) at 10 appropriate intervals on samples stored in loosely covered half-pint jars for 38 weeks at 26.7° C. Capillary melting point (15), Kaufman iodine number (15), refractive index at 48° C. (15), saponification number (1), and smoke point (1) were determined on the fresh material.

The experimental biscuits were prepared by two commercial manufacturers. Processing was carried out according to the formula: 50 lb. of soft wheat flour, 5 lb. of shortening, baking soda (6 oz., Plant *A*; 8 oz., Plant *B*), and water as used in plant practice. Shortenings (described above) and flour used by both manufacturers were obtained from the same sources. The amount of moisture in the biscuits produced was quite uniform, but the fat content was generally higher for Plant *A* products (Table I).

TABLE I

Mean moisture and fat contents of biscuits prepared with four types of shortening in two plants

Biscuit group	No. of samples in group		Fat and moisture contents, %			
			Plant *A*		Plant *B*	
	Plant *A*	Plant *B*	Fat	Moisture	Fat	Moisture
I. Compound animal–vegetable shortenings	4	3	10.4	7.5	7.8	7.1
II. Blended vegetable shortenings	2	2	10.7	6.6	8.4	6.5
III. Hydrogenated vegetable shortenings	6	3	10.2	7.3	8.0	6.6
IV. Stabilized, hydrogenated vegetable shortenings	5	4	10.3	7.3	8.0	6.8

Each lot of biscuits was sampled and ground. Portions of the material (120 gm.) were placed in laminated glassine bags, and each bag was sealed in a No. 1 tin can. This left about one inch of headspace.

Biscuits prepared by Plant *A* with 12 of the 17 shortenings were stored at 26.7°, 43.3°, and 60° C., while those prepared with the five remaining shortenings were stored at 60° C. Biscuits made with the same 12 shortenings at Plant *B* were stored only at 60° C. The plant products were compared at 60° C. because this is the usual temperature employed in the Schaal incubation test for fats and fat-containing materials (6, p. 125). Flavour score of the biscuit, peroxide oxygen value of the extracted fat, and pH of a potassium chloride extract of the biscuit material were determined at each sampling (5).

Samples were taken at 15 suitable intervals during total storage periods of 82, 48, and 30 weeks at temperatures of 26.7°, 43.3°, and 60° C., respectively.

Shortening and biscuit data were examined statistically by means of analyses of variance and by calculation of simple coefficients of correlation.

Results

Shortenings

Group mean values for measured properties are shown in Table II, and peroxide development is further illustrated in Fig. 1.

TABLE II

MEAN VALUES FOR MEASURED PROPERTIES OF 17 BISCUIT SHORTENINGS OF FOUR TYPES

Shortening group	No. of samples in group	Measurements						
		Melting point, ° C.	Iodine No.	Refractive index (at 48° C.)	Saponification No.	Smoke point, ° F.	Swift stability, hr. at 110° C.	Mean peroxide value, ml. of 0.002 *N* thiosulphate per gm. (over all samplings for 38 weeks' storage at 26.7° C.)
I. Compound animal-vegetable	4	45.1	70.5	1.4589	192.7	420	9	126.8
II. Blended vegetable	2	42.5	77.9	1.4591	192.2	426	13	22.9
III. Hydrogenated vegetable	6	43.8	68 1	1.4579	189.9	425	20	11.4†
IV. Stabilized, hydrogenated vegetable	5	43.6	59.0	1.4568	190.8	424	66	0.8‡
Smallest necessary difference between any two groups for statistical significance (5% level)		—	8.9	0.0012	—	—	12	30.9

† *Three shortenings only.*
‡ *Four shortenings only.*

Statistical calculation showed no significant differences in mean value between shortening groups for melting point, saponification number, and smoke point; significant differences for iodine number and refractive index; and highly significant differences for Swift stability and mean peroxide value. Group IV shortenings were lower in iodine value than those of Groups I, II, and III and lower in refractive index than those of Groups I and II. Swift stability was higher for Group IV than for the other three groups and mean peroxide value was higher for Group I than for the other three.

Iodine number, refractive index, Swift stability, and log mean peroxide value were interrelated (Table III). Low iodine number was associated with low refractive index and high stability. Saponification number was inversely related to smoke point.

TABLE III

SIMPLE COEFFICIENTS OF CORRELATION BETWEEN MEASURED PROPERTIES OF BISCUIT SHORTENINGS

Quantities correlated	Saponification No.	Iodine No.	Smoke point	Refractive index	Melting point	Swift stability
Iodine No.	.11	—	—	—	—	—
Smoke point	— 52*	—.01	—	—	—	—
Refrăctive index	.11	.77**	.14	—	—	—
Melting point	—.17	—.09	.12	.11	—	—
Swift stability	— 30	—.63**	.16	— 61**	—.10	—
Log mean peroxide value†	.31	.69*	—.28	.74**	.18	—.82**

† *Twelve values; all other measurements,* 17 *values.*
* *Indicates* 5% *level of statistical significance.*
** *Indicates* 1% *level of statistical significance.*

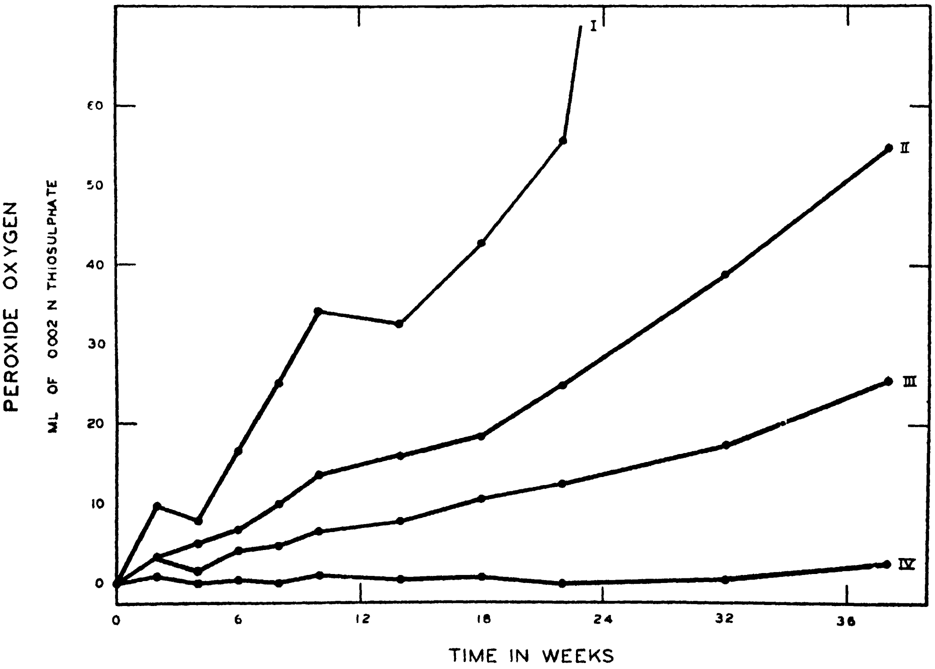

FIG. 1. *Mean peroxide oxygen development in shortenings of four types stored at 26.7° C. for 38 weeks. I, compound animal–vegetable; II, blended all-vegetable; III, hydrogenated vegetable; IV, stabilized, hydrogenated vegetable.*

The results indicate that stability was a function of shortening type. Differences in shortening stability were apparently maintained during storage (Fig. 1). Stabilization of Group IV shortenings was evidently due in part to hydrogenation to a low iodine number, while the inferior keeping quality of Group I material was presumably caused by the presence of animal fat.

Biscuits

Mean values over all sampling periods for flavour, peroxide oxygen, and pH measurements on biscuits made with each of the four types of shortening are presented in Table IV.

There were no statistically significant differences in mean pH and peroxide measurements at any of the storage temperatures and no differences in flavour score of material stored at 60° C. Significant group differences in flavour score were present in biscuits stored at 43.3° C., and highly significant differences in biscuits stored at 26.7° C. The mean flavour score for Group I biscuits was lower than the means of Groups II, III, and IV for storage temperature 26.7° C., and lower than the means of Groups III and IV for storage temperature 43.3° C.

The marked inferiority in keeping quality of Group I biscuits and the lack of differentiation among the other three groups is illustrated by the flavour changes shown in Fig. 2. The effect of storage temperature on mean flavour values averaged over all shortenings is shown in Fig. 3 (Plant *A* biscuits only). It was estimated that ration biscuits prepared with a good grade of hydrogenated vegetable shortening had average storage lives of 84, 22, and 13 weeks at 26.7° C., 43.3° C., and 60° C., respectively.

The chemical measurements yielded only limited information about keeping quality. Pronounced peroxide oxygen development was found only in biscuits prepared with compound animal–vegetable and blended all-vegetable shortenings and stored at 26.7° C. (Fig. 2). There was an initial decline in pH which was much more rapid at the higher storage temperatures (Fig. 3).

Association between mean biscuit flavour and mean peroxide oxygen content of stored shortening was negative, and closer for the lower biscuit storage temperatures (Table V). The relation between peroxide oxygen values for biscuits and for stored shortenings was not significant.

Mean biscuit flavour at 26.7° C. did not increase appreciably with the use of shortenings having Swift stabilities greater than 40 hr. at 110° C. (Fig. 4). A similar relation for Swift stability of shortenings and mean peroxide oxygen content of biscuits held at 26.7° C. is also shown in Fig. 4. Shortening stability and biscuit flavour score were more markedly associated at the lower storage temperatures (Table V). Log Swift stability and mean biscuit peroxide value at 26.7° C. were also related.

Useful storage life of the biscuits was held to be at an end when the flavour score fell to five palatability units (5). Estimated storage lives of the various

TABLE IV

MEAN VALUES OVER ALL SAMPLINGS FOR FLAVOUR SCORES, AND pH AND PEROXIDE OXYGEN VALUES OF RATION BISCUITS STORED AT 26.7°, 43.3°, AND 60° C., FOR 82, 48, AND 30 WEEKS, RESPECTIVELY

Biscuit group	No. of samples in group		Flavour score				pH				Peroxide oxygen value, ml. of 0.002 thiosulphate per gm. of fat			
			Plant *A*			Plant *B*	Plant *A*			Plant *B*	Plant *A*			Plant *B*
	Plant *A*, 60° C.	All others	26.7° C.	43.3° C.	60° C.	60° C.	26.7° C.	43.3° C.	60° C.	60° C.	26.7° C.	43.3° C.	60° C.	60° C.
I. Compound animal-vegetable shortenings	4	3	4.9	4.6	5.3	5.5	8.1	7.7	7.2	7.6	23.3	7.3	1.5	0.3
II. Blended vegetable shortenings	2	2	6.2	5.1	5.3	5.7	7.9	7.5	7.2	7.5	31.8	6.9	1.4	0.2
III. Hydrogenated vegetable shortenings	6	3	6.1	5.7	5.5	5.8	7.9	7.6	7.2	7.5	10.5	1.7	0.3	0.1
IV. Stabilized, hydrogenated vegetable shortenings	5	4	6.4	5.8	5.4	5.7	8.0	7.6	7.2	7.5	3.3	1.1	0.4	0.1
Smallest necessary difference between any two groups for statistical significance (5% level)			0.8	0.9	—	—	—	—	—	—	—	—	—	—

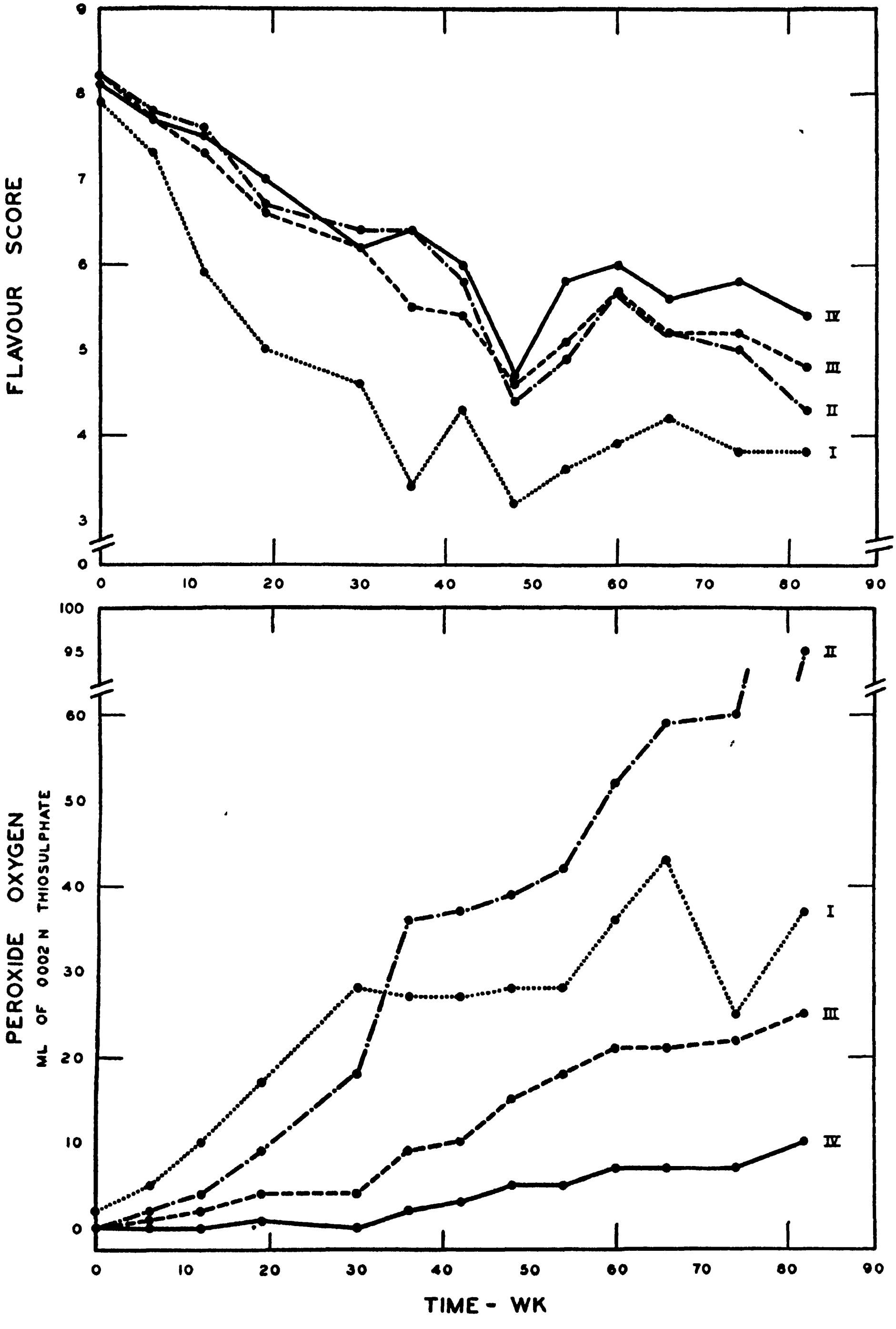

FIG. 2. *Changes in mean flavour score and peroxide value for biscuits stored at 26.7° C. and prepared with four shortening types: I, compound animal-vegetable; II, blended all-vegetable; III, hydrogenated vegetable; IV, stabilized, hydrogenated vegetable.*

groups of biscuits under the storage conditions studied are given in Table VI. Calculations based on these data supported the previous conclusions, namely, that a high level of biscuit keeping quality was obtained by the use of a reasonably stable shortening, but further increase in biscuit life was not obtained by the use of shortenings of still greater stability.

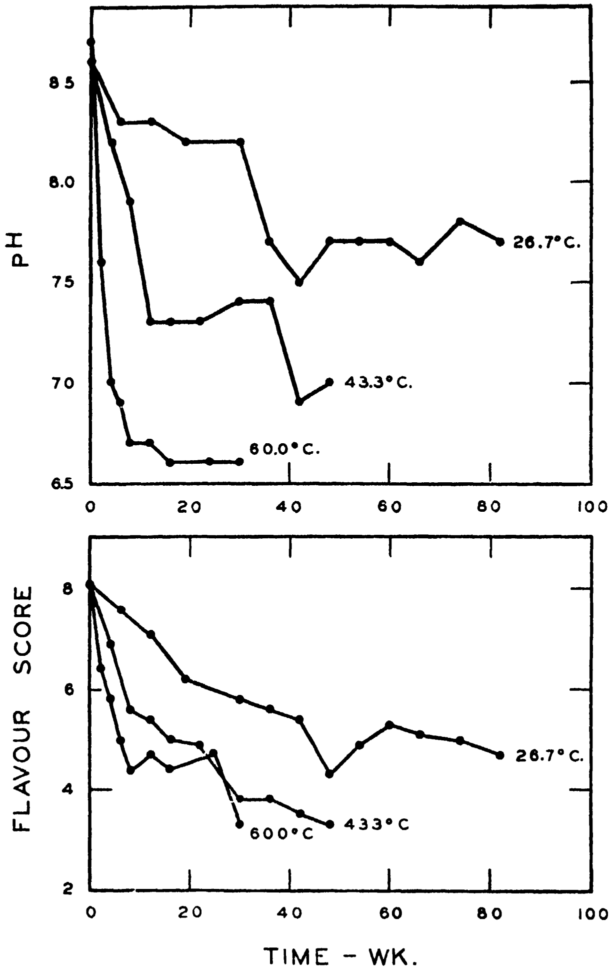

FIG. 3. *Changes in mean flavour score and pH value, over all shortenings used, for biscuits stored at 26.7°, 43.3°, and 60.0° C. (Plant A only).*

No conclusion could be drawn regarding plant practice, as the storage temperature (60° C.) at which the two plant products were compared was the one at which differentiation among biscuit groups was least pronounced. The use of different quantities of baking soda (8, 10) and the variation found in fat concentration (5), together with differences in processing procedure, probably accounted for differences between the plant products.

TABLE V

CORRELATION OF SHORTENING STABILITY WITH BISCUIT STABILITY

Quantities correlated			Correlation coefficient
Mean peroxide values of 12 stored shortenings (26.7° C.) with:			
Plant *A*	Mean biscuit flavour,	26.7° C.	−.92**
		43.3° C.	−.74**
		60° C.	−.55*
	Mean biscuit peroxide value,	26.7° C.	.53
Plant *B*	Mean biscuit flavour,	60° C.	−.56*
Log Swift stability (110° C.) of 12 shortenings with:			
Plant *A*	Mean biscuit flavour,	26.7° C.	.78**
		43.3° C.	.81**
		60° C.	.56*
	Mean biscuit peroxide value,	26.7° C.	−.78**
Plant *B*	Mean biscuit flavour,	60° C.	.21

* *Indicates 5% level of statistical significance.*
** *Indicates 1% level of statistical significance.*

Discussion

Shortenings

Mean iodine numbers of 75.2 for 11 samples of mixed animal-vegetable shortening, 78.2 for 31 samples of blended all-vegetable shortening, and 69.9 for 60 samples of hydrogenated vegetable shortening have been reported (2). These figures are somewhat higher than those reported here. An examination of smoke points determined by other workers (14) shows a comparable average of 422° F. for 10 vegetable shortenings.

None of the correlations estimated was sufficiently close for prediction purposes, although a number of anticipated associations were found. An association of melting point with iodine value was not expected in a selection of shortenings differing so widely in composition. Decrease in smoke point with increase in saponification value may have been due to variation in free fatty acid content (7, vol. 1, p. 394) or variation in content of component acids of low molecular weight (3, p. 68).

Biscuits

The investigation demonstrated that values for chemical measurements and flavour tests obtained for ration biscuits stored at the usual temperature of 60° C. (6, p. 125) may be misleading if they are used to predict storage behaviour at lower temperatures.

An explanation of the low peroxide value of extracted fat at the higher storage temperatures is possible if it is assumed that breakdown of peroxides proceeded simultaneously with their formation, and that the relative rate of peroxide decomposition was greater at the higher temperatures. The more rapid initial decline in pH at the higher temperatures would support this, if the lowering of pH was entirely due to formation of free fatty acids from peroxide breakdown. However, pH changes might be attributable in part to changes in protein constituents, and it is also possible that decomposition products of proteins inhibited peroxide formation in the fat fraction, particularly at 60° and 43.3° C. Baking operations and the influence of non-fat constitutents in the biscuit were apparently responsible for the lack of close association between peroxide oxygen values of shortenings stored at

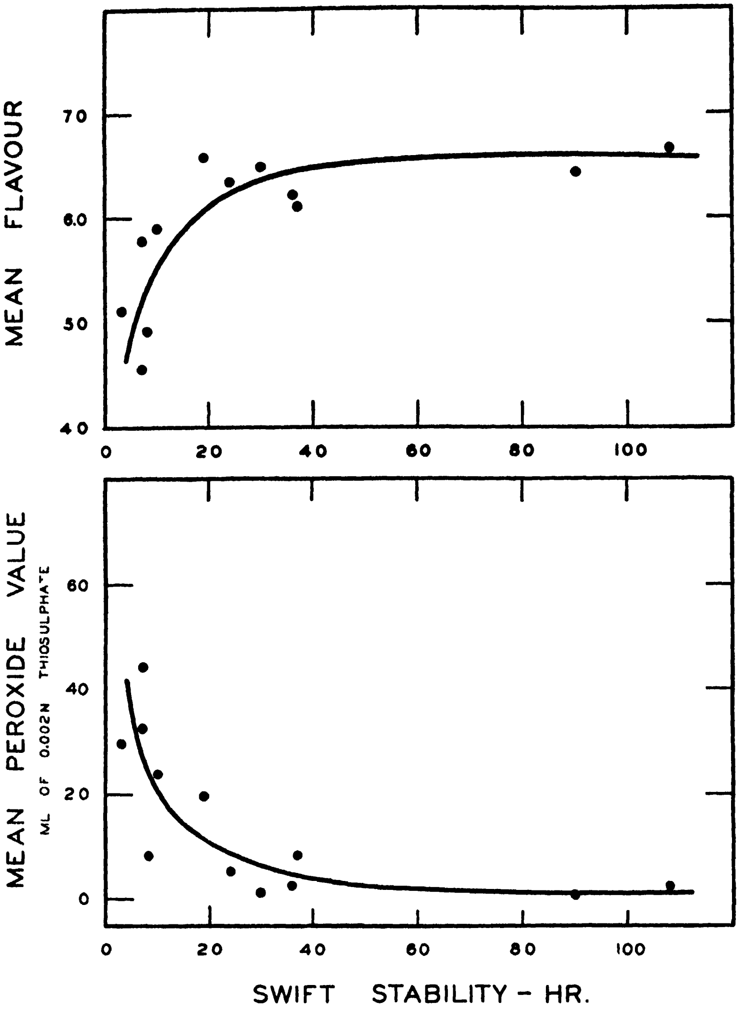

FIG. 4. *Relation of Swift stability (110° C.) of shortenings to mean flavour score and mean peroxide value of biscuits stored at 26.7° C.*

TABLE VI

ESTIMATED MEAN STORAGE LIFE (TIME FOR FLAVOUR SCORE TO REACH A VALUE OF FIVE) OF RATION BISCUITS STORED AT 26.7°, 43.3°, AND 60° C.

Biscuit group	No. of samples in group		Storage life, weeks			
			Plant *A*			Plant *B*
	Plant *A*, 60° C.	All others	26.7° C.	43.3° C.	60° C.	60° C.
I. Compound animal–vegetable shortenings	4	3	19	7	6	8
II. Blended vegetable shortenings	2	2	63	14	7	13
III. Hydrogenated vegetable shortenings	6	3	67	20	7	17
IV. Stabilized, hydrogenated vegetable shortenings	5	4	97	23	7	17

26.7° C. and peroxide oxygen values of the same fat extracted from biscuits also stored at that temperature. Difference in peroxide development under the two conditions was most marked for the blended all-vegetable shortenings (cf. Figs. 1 and 2).

Although peroxide values for biscuits stored at 26.7° C. and prepared from compound animal–vegetable (Group I) and blended vegetable (Group II) shortenings were both high, biscuits containing the all-vegetable product were rated as having higher mean flavour. This was presumably due to the greater stability of peroxides formed in vegetable fat, as compared to those formed in animal fat, with a corresponding delay in liberation of objectionable products of peroxide breakdown (11).

Acknowledgments

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CHARACTERISTICS OF CANADIAN LARD[1]

By H. J. Lips[2*] and G. A. Grant[3]

Abstract

Mean values for measured properties of 33 samples of lard obtained from 26 packing plants across Canada were: iodine number, 58.7; saponification number, 193.9; melting point, 43.5° C.; smoke point, 382° F.; colour, 8.8Y, 1.6R; unsaponifiable matter, 0 43%; fatty acid composition: saturated, 45.6%, oleic, 44.7%, linoleic, 8.7%, linolenic, 0.6%, arachidonic, 0 4%; storage life at 26.7° C., 9 2 weeks; Swift stability, 3 5 hr.; iodimetric peroxide, 1.6 ml. of 0.002 *N* thiosulphate per gm.; ferrometric peroxide, 9.7 m.e. per kgm.; Kreis test, 9.9; Stamm test, 2.3; alpha-dicarbonyl test, 3.4; free fatty acid, 0.4%; fluorescence, 79.2. The distribution of values is shown by histograms.

Simple correlation coefficients computed between measured properties showed the following to be associated: melting point with iodine number; free fatty acid content with melting point, smoke point, and red colour; storage life at 26.7° C. with log of Swift stability and initial ferrometric peroxide, Kreis, and alpha-dicarbonyl values.

Introduction

In pre-war years there was usually a lard surplus because the housewife preferred hydrogenated vegetable shortening to the animal product. The factors that have contributed to the inferior competitive position of lard are: lack of resistance to spoilage, lack of blandness, and unsuitability for use in deep-fat frying due to a low smoke point (28, 42). However, in pastry the shortening power of lard is often superior to that of hydrogenated vegetable oils (41, 58).

In the United States, progress has been made in the development of bland lards that may be kept for extended periods without refrigeration. These products owe their desirable characteristics to special processing, including: deodorization, partial hydrogenation, addition of hardened lard "flakes", or the incorporation of antioxidants such as gum guaiac and lecithin (44, 49, 61). In Canada, although the Food and Drugs Act has been amended to permit the incorporation in lard of certain antioxidants, commercial stabilization under the Act has not begun. Provided that additions are indicated on the container and that not more than 0.2% of stabilizing material is added, singly or in combination, the following substances may now be used: gum guaiac; vegetable oil containing tocopherols; lecithin; citric, tartaric and ascorbic acids (12).

Formerly Canada imported over 50% of her fats and oils requirements, exclusive of butter (35). During the war, the lard industry expanded, owing to a large increase in hog production and to emergency salvage and carcass

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trimming operations. It is expected that there will be an eventual surplus of lard, and one of the problems confronting the Canadian packing industry will be the improvement of this product so that high levels of export and domestic consumption can be maintained in the face of post-war competition by shortenings prepared from vegetable oils.

As a basis for proposed work to improve the quality of Canadian lard, it was considered advisable to determine the characteristics of the product as freshly produced. Surveys of Canadian lard were conducted as early as 1888 by the Food and Drugs laboratory (then a branch of the Department of Inland Revenue), but these were concerned only with adulteration of lard in respect to other fats and excess moisture (30).

A preliminary examination of market samples obtained in the city of Ottawa in the summer of 1944 showed an average keeping time of only five weeks at 26.7° C. With this indication of stability as a guide a more extensive survey of available commercial products was begun in September, 1944. Questionnaires concerning plant practice were submitted to Canadian packing houses, and representative samples of processed material were requested.

Materials and Methods

A total of 33 samples of lard was obtained from 26 packing plants across Canada and stored at −40° C. until required. Of these samples 12 were dry rendered and 21 wet rendered. As indicated in replies to questionnaires, the details of processing procedure varied considerably from plant to plant.

The product was characterized by determination of Kaufmann iodine number (14, 26); saponification number (24); capillary melting point (5); unsaponifiable matter (2); oleic, linoleic, linolenic, and arachidonic acids (9); smoke point (2); Lovibond colour (2); free fatty acid (32); and Swift stability* (27, 40). Organoleptic storage life at 26.7° C.; iodimetric and ferrometric peroxide oxygen; Kreis, Stamm, and alpha-dicarbonyl tests; and fluorescence were determined by methods reviewed elsewhere (18).

Results and Discussion

It was necessary to respect the confidential nature of some of the data obtained from the questionnaires but the majority of the laboratory results are reported (Fig. 1 and Table I). Initial odour is not given, but should be mentioned because many samples were objectionable in varying degree, having definite 'porky', 'tankage', or 'burnt' odours. Lovibond blue reading and initial iodimetric peroxide content are not represented graphically, as the results included a number of zero values. No histogram for arachidonic acid concentration is given because the variation in value was slight.

* *When the indicator method (40) is used to determine Swift stability, the indicator should be renewed after the volatile fatty acids originally present have been driven off. This should not take longer than 30 min.*

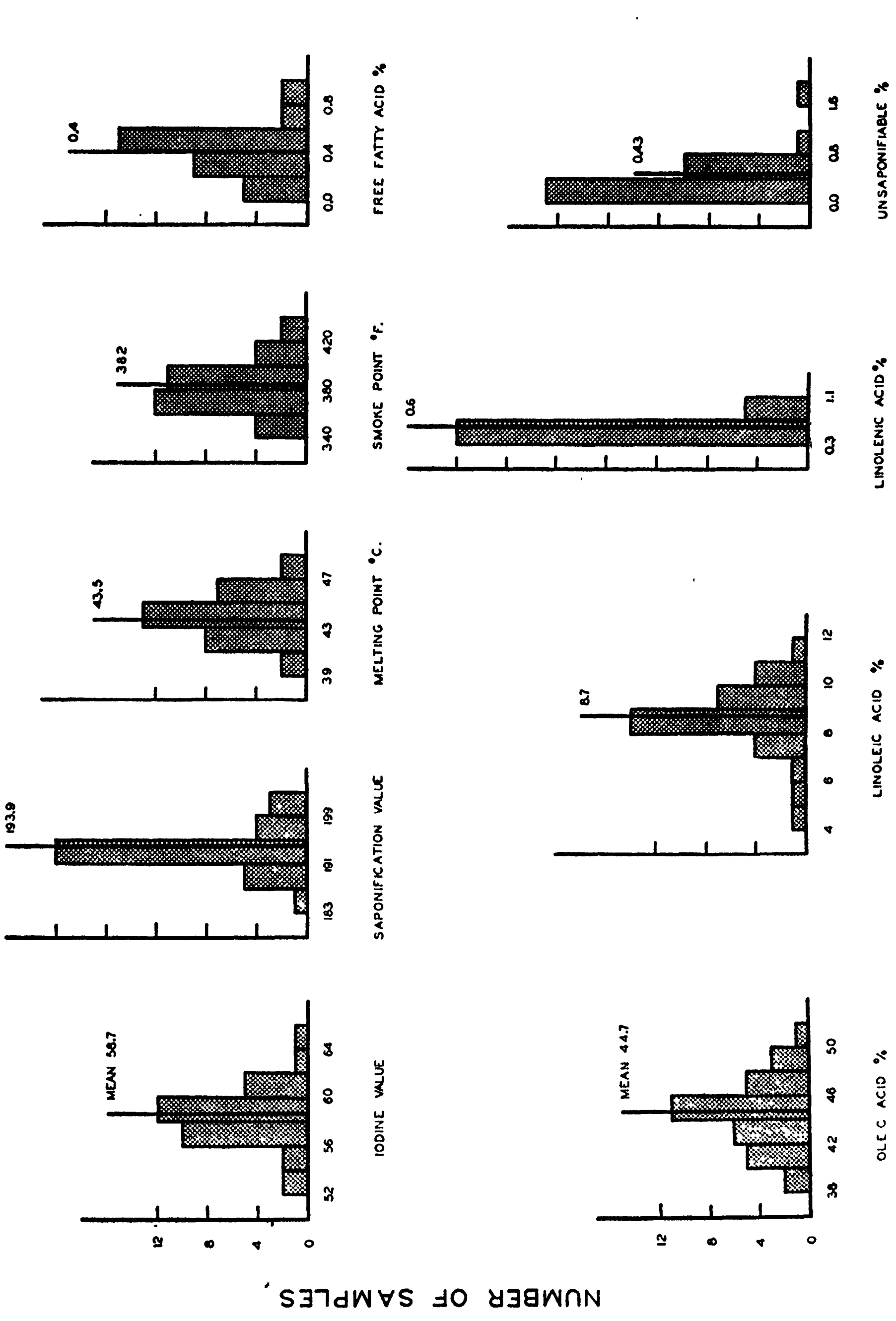

FIG. 1*a*. *Distribution of measured properties of Canadian lard.*

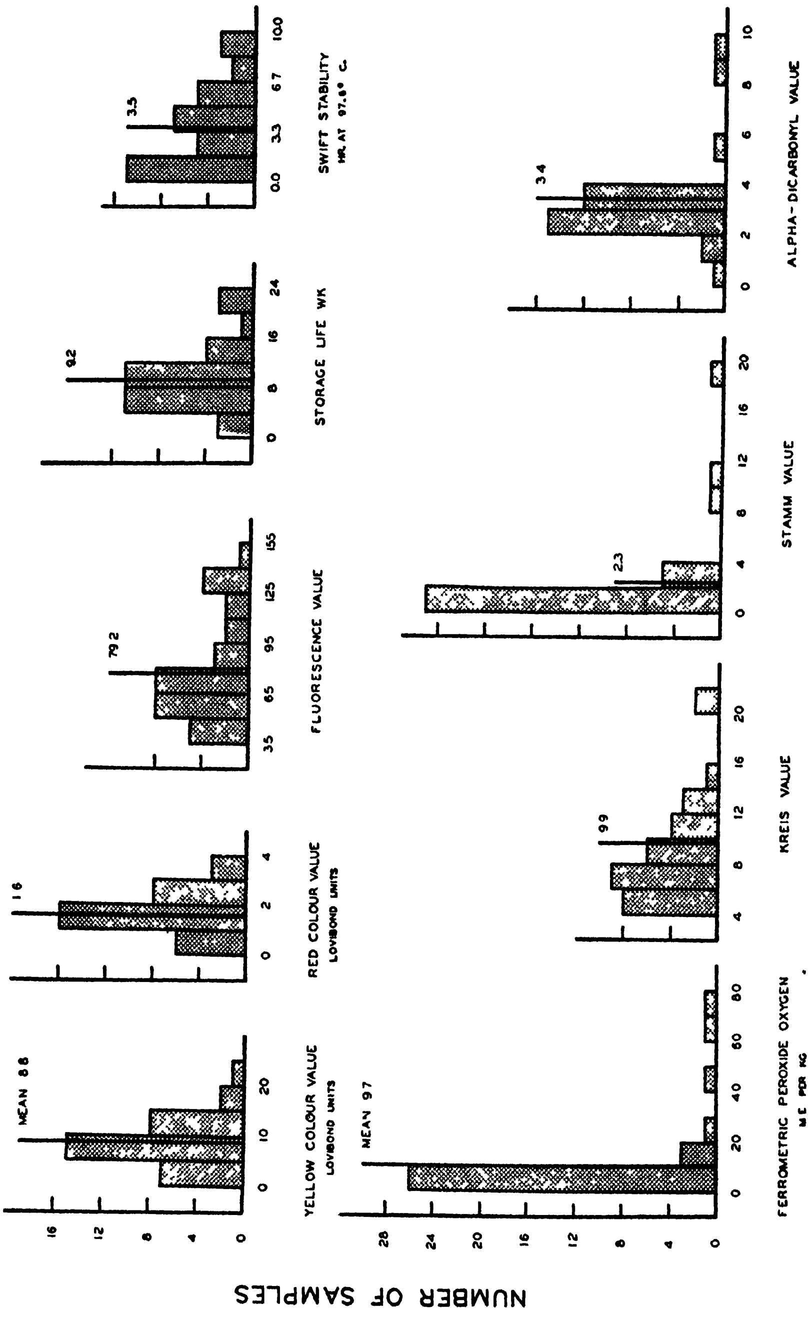

FIG. 1b. *Distribution of measured properties of Canadian lard.*

TABLE I

MEAN VALUES AND RANGES FOR MEASURED PROPERTIES OF CANADIAN LARD

Measurement	Mean	Range	Measurement	Mean	Range
Iodine number	58.7	53.1–65.3	Swift stability, hr. at 97.8 °C.	3.5	0.3–9.0
Saponification number	193.9	184.2–202.2			
Melting point, °C.	43.5	39.3–47.9	Ferrometric peroxide, m.e. per kgm.	9.7	0.0–73.2
Smoke point, °F.	382	345–438			
Yellow colour, Lovibond units	8.8	3.0–22.3	Iodimetric peroxide, ml. of 0.002 *N* thiosulphate per gm.	1.6	0.0–14.2
Red colour, Lovibond units	1.6	0.4–3.1			
Blue colour, Lovibond units	0.2	0.0–1.2	Kreis test, extinction coefficients	9.9	3.7–20.7
Saturated acids*, %	45.6	—			
Oleic acid*, %	44.7	38.6–51.8	Stamm test, extinction coefficients	2.3	0.0–19.9
Linoleic acid*, %	8.7	4.6–11.3			
Linolenic acid*, %	0.6	0.4–1.1	Alpha-dicarbonyl test, extinction coefficients	3.4	0.8–9.9
Arachidonic acid*, %	0.4	0.3–0.5	Free fatty acid, as % oleic	0.4	0.1–0.9
Unsaponifiable matter, %	0.43	0.20–1.70			
Storage life, weeks at 26.7° C.	9.2	2.0–22.0	Fluorescence, photofluorometer units	79.2	39.8–146.0

**Expressed as % of total acids.*

Characteristics of Canadian Lard

Values for iodine number, saponification number, and melting point had a fairly normal distribution (Fig. 1). Variation in these values, in the absence of adulteration or advanced spoilage, would seem to be chiefly due to differences in the original fat before processing.

There was appreciable variation in oleic, linoleic, and linolenic acid concentrations as determined spectrophotometrically. Saturated acid values were obtained by difference only. Here again the differences were concerned with the original raw materials.

Values for unsaponifiable matter vary to some extent with the method of rendering the lard, and large variations may affect the values obtained for other measurements on the whole fat (36, pp. 401, 425). The values greater than 0.8% are unusually high.

It is considered that the smoke point of lard should be at least 400° F. to compete with that of shortening, since a survey of 17 wartime shortenings, including animal–vegetable compounds, showed a mean value of 424° F. (39).

For several samples it was necessary to remove suspended material by filtration before colour measurements could be made. Blue readings were obtained for 10 of the 33 samples, and it was found that the presence of carbon in suspension markedly increased the apparent blue colour. Variation in colour would appear to be chiefly governed by factors of processing technique.

Stability of most of the lard samples was poor, as estimated by storage life at 26.7° C. and by Swift stability at 97.8° C. The magnitude of these measurements depends on the nature of the original material and the details of processing procedure, if it is assumed that no antioxidants were used.

The values for iodimetric peroxide, ferrometric peroxide, Kreis test, Stamm test, alpha-dicarbonyl test, and free fatty acid reflect the degree of exposure of the lard during processing to spoilage by biological and chemical action. Considerable variation in these respects is shown in Table I and Fig. 1. Fluorescence values were unevenly distributed.

Interrelation of Measured Properties

The literature contains a number of references to relations between various measured properties of fats and oils. Iodine value is reduced by marked oxidation (33, p. 95; 36, p. 425), saponification number is influenced to some extent by free fatty acid content (36, p. 394), and melting point is appreciably altered by changes in free fatty acid (36, p. 329). Moisture content, by affecting lard transparency, may influence estimation of the capillary melting point (17; 36, p. 288). However, according to the Canadian Food and Drugs Act (12), moisture content of lard is limited to 1%, and the product must be free from rancidity. In the absence of changes in composition, smoke point varies inversely with free fatty acid content (7; 23, pp. 132-136).

In the present study the relation of measured properties to one another was investigated by calculating simple coefficients of correlation, except where this was precluded by the presence of a large number of zero values, as in the case of iodimetric peroxide and Lovibond blue measurements. Most of the correlations proved to be insignificant; only the more important ones are reported (Table II).

Iodine number was inversely related to melting point, but no association of saponification number with other measured properties was found. The significant association of melting point with free fatty acid content indicates that the free fatty acids formed before or during processing lowered the melting point.

Smoke point, Lovibond red colour, and free fatty acid content were all interrelated. High values for free fatty acid were associated with low smoke point and high red colour. Lowering of the smoke point by free fatty acids is a well recognized effect, and significant correlations have been reported (42). The relation of free fatty acid to red colour suggests that there was a parallel increase in these two measurements during processing. Red and yellow colour readings were directly related.

The correlation of storage life at 26 7° C. with log Swift stability (Fig. 2) indicates that the latter determination has certain usefulness in the prediction of lard keeping quality at lower temperatures, at least in the absence of added antioxidants. There has been some question about this point (51). Storage life varied inversely with ferrometric peroxide, Kreis and alpha-dicarbonyl values; that is, samples with high values for these chemical measurements had short storage lives, as oxidative deterioration was already in progress. Iodine value, content of saturated and unsaturated acids and unsaponifiable matter, and fluorescence had no observed important relation to storage life. The results support a previous suggestion that degree of unsaturation in pigs' fat is not necessarily the limiting factor in determining stability (34, pp. 60-64).

Other relations examined between measured properties were not significant.

TABLE II

COEFFICIENTS OF CORRELATION BETWEEN MEASURED PROPERTIES OF CANADIAN LARD

Quantities correlated	No. of values	Correlation coefficient
Iodine number with:		
Melting point	33	− .41*
Melting point with:		
Smoke point	33	.41*
Lovibond yellow	33	− .29
Lovibond red	33	− .24
Free fatty acid	33	− .59**
Smoke point with:		
Lovibond yellow	33	− .19
Lovibond red	33	− .38*
Free fatty acid	33	− .87**
Lovibond yellow with:		
Lovibond red	33	.82**
Lovibond red with:		
Free fatty acid	33	.41*
Storage life with:		
Log Swift stability	29	83**
Ferrometric peroxide	26	− 63**
Kreis test	29	− 39*
Stamm test	27	− .28
Alpha-dicarbonyl test	27	− .36*

* *Indicates 5% level of statistical significance.*
** *Indicates 1% level of statistical significance.*

Relation of Measured Properties to Plant Practice

Stability and smoke point were considered likely to be altered by variations in processing procedure, so the effect of these variations upon storage life and smoke point was assessed on wet and dry rendered lards considered together and separately (Table III). However, the calculated correlation of any one plant practice with the measured properties is not strictly valid, as all other factors were not constant among plants. Moreover the calculations are based on a limited number of values, and the results may not reflect general operational experience in all cases.

A preliminary analysis of variance demonstrated no important difference in mean storage life between wet and dry rendered lard, but showed that the mean smoke point for dry rendered lard was significantly higher than for the wet rendered product. The latter result is attributable to the higher free fatty acid content of the wet rendered fats, due to their exposure to the hydrolyzing effect of long contact with steam or hot water.

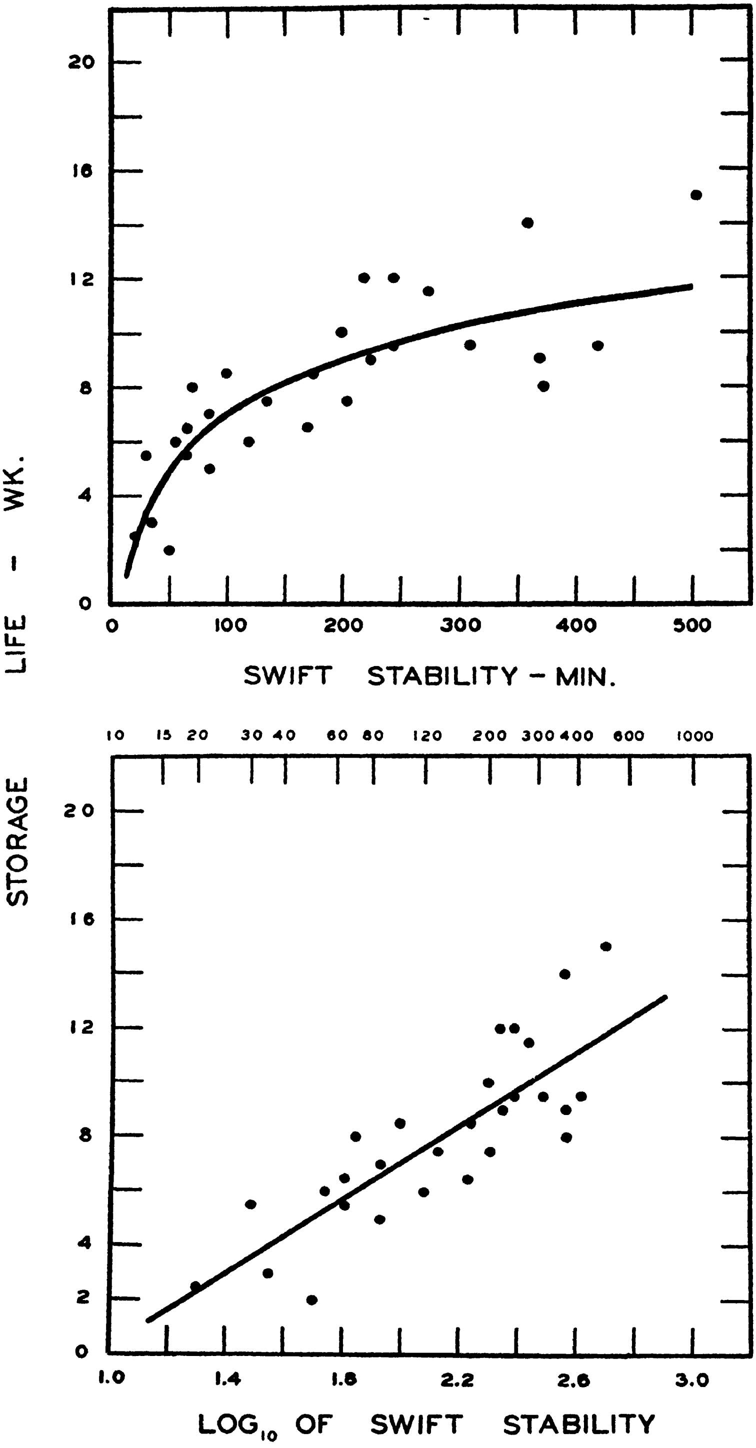

FIG. 2. *Relation of Swift stability at 97.8° C. to storage life at 26.7° C. for Canadian lard.*

TABLE III

COEFFICIENTS OF CORRELATION BETWEEN PLANT PRACTICES AND MEASURED PROPERTIES FOR CANADIAN LARD

Quantities correlated	No. of values			Correlation coefficients		
	Wet rendered lard	Dry rendered lard	Total	Wet rendered lard	Dry rendered lard	Total
Storage life with:						
Killing fat, %	21	12	33	.15	.10	.14
Cutting fat, %	21	12	33	− .14	− .35	− .23
Bones, %	21	12	33	.77**	− .15	− .22
S.P.† material, %	21	12	33	− .02	− .31	− .11
Rendering temperature	21	12	33	.41	− .30	− .12
Rendering time	3	11	14	− .42	.69*	− .02
Deodorizing temperature	—	4	5	—	.00	− .40
Deodorizing time	—	4	5	—	− .70	.08
Filtering temperature	20	11	31	− .31	− .43	− .32
Time, processing to packaging	21	12	33	.10	− .30	− .12
Smoke point with:						
Killing fat, %	21	12	33	− .77**	.52	− .19
Cutting fat, %	21	12	33	− .15	.22	− .09
Bones, %	21	12	33	.40	.53	.33*
S.P.† material, %	21	12	33	− .03	.20	.11
Rendering temperature	21	12	33	.33	.82**	.51**
Rendering time	3	11	14	.99*	− .56	− .71**
Deodorizing temperature	—	4	5	—	− .88	− .45
Deodorizing time	—	4	5	—	− .83	− .42
Filtering temperature	20	11	31	.32	− .12	− .22
Time, processing to packaging	21	12	33	− .10	.19	− .08

† *Sweet pickle.*
* *Indicates 5% level of statistical significance.*
** *Indicates 1% level of statistical significance.*

The storage life of wet rendered lard appeared to be lengthened by increase in amount of bones (Table III), presumably because of their content of natural stabilizing substances. The presence of 0.14% lecithin in pig-bone fat as compared to 0.04 to 0.06% in lard has been reported (25). With the dry rendered lard, increase in rendering time appeared to be beneficial. This may be related to better extraction of natural stabilizers from the non-fatty material. Although correlations of storage life with filtering temperature failed to attain statistical significance, they were all negative, indicating that moderately low filtering temperatures (160° to 170° F.) would be desirable for the production of more stable lard.

High smoke point was favoured by decrease in killing fat in wet rendering, and by an increase in bones. A negative correlation of smoke point with cutting fat rather than killing fat had been anticipated, since the former fat usually has more time to develop free fatty acids by enzymic action before it is rendered (23, pp. 132–136; 37, 45, 60). Similarly it was expected that increase in bones might lower the smoke point, since these may stand for some time before rendering, with consequent development of free fatty acids in the fat that they carry. No satisfactory explanation can be offered for these discrepancies at present because of limited information about the operations concerned. The relation between smoke point and rendering temperature was positive, and between smoke point and rendering time negative. This suggests that rendering should be carried out at a relatively high temperature in as short a time as possible (23, pp. 132–136; 43, 55).

Although none of the other relations tabulated was significant, reduction in deodorizing temperatures and times used appeared to be desirable. In general the influence of processing procedures upon wet and dry rendered products was dissimilar.

Comparison with Lards from Other Countries

Extensive control examinations of lard in other countries have been reported (1, 13).

Comparative figures in the literature on the composition of lard are largely based on chemical rather than spectrophotometric measurements. For 27 American lards (4), the calculated compositions were predicated on the absence of fatty acids more unsaturated than linoleic (Table IV). However, the presence of linolenic, unsaturated C_{20-22}, and conjugated acids has been demonstrated (10; 31; 21, pp. 80–86). The presence of arachidonic acid is used as the basis of a spectrophotometric method for distinguishing between lard and hydrogenated vegetable oils (6). The greater unsaturation of other lards as compared to Canadian lards is undoubtedly due in part to differences in the nature and fat content of the diet of the hog (33, pp. 17–26). Changes in the diet similarly affect melting point, but have less effect on saponification number.

Comparative figures for lard colour have not been found in the literature. Authentic blueness in lard is said to be due to a natural pigment, and is considered an indication of careful processing rather than poor handling.* The blue pigment is unstable, and on oxidation it changes to red, or a mixture of red and yellow (23, pp. 157–158). Its presence is objectionable, since the consumer prefers whiteness.

The smoke point figure quoted in Table IV for American samples does not include the value given for a bland lard (59).

Available figures for small numbers of American samples indicate that lard usually has indifferent keeping quality unless it is stabilized by the addition of antioxidants, or subjected to special processing treatments (50).

The use of fluorescence in the study of fats to detect impurities and deterioration has been suggested by several workers (19, 20, 47, 54) but no recent data are available for comparison. Fluorescence in lard is said to depend both on state of preservation and manner of processing (8, 16, 48, 53).

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* *Anon. National Provisioner, 112(20): 15. 1945.*

TABLE IV

A COMPARISON OF VALUES FOR MEASURED PROPERTIES OF CANADIAN LARD WITH OTHER REPORTED AND RECOMMENDED VALUES

Measurement	Comparative values			
	Canadian		American	Other
	Mean	Range		
Iodine number	58.7	53.1–65.3	27 samples, 64.6 (4) Recommended, 46–70 (3)	General, 46–66 (22, p. 136) English, 108 samples, 57–73 (56) Portuguese, 30 samples, 63.9 (46)
Saponification number	193.9	184.2–202.2	Recommended, 195–202 (3)	General, 193–200 (22, p. 136) Portuguese, 30 samples, 195.8 (46)
Melting point, °C.	43.5	39.3–47.9	—	General, 28–48 (22, p. 136)
Smoke point, °F.	382	345-438	6 samples, 371 (59)	—
Saturated acids*, %	45.6	—	27 samples, 36.8 (4)	Portuguese, 30 samples, 38.5 (46)
Oleic acid*, %	44.7	38.6–51.8	27 samples, 51 5 (4)	Portuguese, 30 samples, 49 2 (46)
Linoleic acid*, %	8.7	4.6 11.3	27 samples, 11.7 (4)	Portuguese, 30 samples, 12.5 (46)
Arachidonic acid*, %	0.4	0.3 0.5	0.02–0.21 (15) 0.31–0.40 (11) 0.2 –0.6 (6)	
Unsaponifiable matter, %	0.43	0.20–1 70	Recommended, 1.0 max. (3)	General, 0.2–0.4 (22, p. 136; 29, p. 135) Portuguese, 30 samples, 0.14 (46)
Swift stability, hr. at 97.8 °C.	3.5	0.3–9.0	7 samples, 5.3 (50)	Other Canadian, 14 samples, 2.2 (38, 40)
Iodimetric peroxide, ml. of 0.002 *N* thiosulphate per gm.	1.6	0.0–14.2	4 samples, 1.5 (28) 6 samples, 0.7 (52) Recommended, 2.5 ml. max. (3)	—
Free fatty acid, as % oleic	0.4	0.1 0.9	6 samples, 0.26 (59) 5 samples, 0.29 (28) 3 samples, 0.33 (57) 4 samples, 0.35 (28) Recommended, 1% max. (3)	General, 0.2- 0.7 (22, p. 136)

* *Expressed as % of total acids.*

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STUDIES COMPARING THE SANITIZING EFFICIENCIES OF HYPOCHLORITES AND QUATERNARY AMMONIUM COMPOUNDS[1]

By C. K. Johns[2]

Abstract

The germicidal speed of four quaternary ammonium compounds has been compared with that of two hypochlorites against *Staphylococcus aureus*, *Bacillus panis* (vegetative cells and spores), *Micrococcus candidus*, cheese starter organisms, *Escherichia coli* and *Pseudomonas aeruginosa*, using the glass slide technique originally devised for comparing chlorine sterilizing agents. Against the Gram-positive species, the quaternary compounds were generally more effective than the hypochlorites; against the Gram-negative species, the reverse held true. Cheese starter organisms were an exception, being killed faster by the hypochlorites. Three of the four quaternary compounds were closely comparable in efficiency, while the fourth was definitely slower. The hypochlorites responded much more readily to favourable adjustments in pH and temperature than did the quaternary compounds. Some bacteriostatic effect was observed with higher concentrations of all four quaternary compounds, but it is not believed that the results were significantly affected thereby. The glass slide technique appears to offer many advantages in the evaluation of the germicidal efficiency of products designed for sanitizing metal or glass surfaces in food processing plants.

Introduction

During the past decade, a large number of 'surface active' detergents have been developed. Of these, the quaternary ammonium compounds have been reported to be particularly effective as germicides (2, 8, 9, 10, 12, 13, 23, 27). Among other uses they are being recommended to supplant hypochlorites for the sanitizing of equipment in the dairy and food industries. So far, however, the only direct comparison of their effectiveness with that of hypochlorite has been reported by Jamieson and Chen (14) in the sanitizing of milk cans. Unfortunately the quaternary compounds were employed at a much higher concentration than the hypochlorite, rendering comparisons difficult. The present studies were designed to afford a direct comparison between representatives of both types of germicide.

In the sanitizing of washed food-handling equipment, the bacteria present on the surfaces of such equipment are often protected by a slight film of diluted milk or other organic material. Tests conducted along the lines of the conventional phenol coefficient determination, in which the test organisms are freely suspended in a solution of the product under test, do not even remotely approximate the conditions under which the sanitizing agent must work in practice. To overcome this objection, when studying the comparative germicidal efficiency of chlorine compounds (19, 20), a 'glass slide' technique was evolved in which the test organisms were present in a partially dried film of diluted skim-milk on the surface of a microscopic slide. This

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technique had shown satisfactory reproducibility with chlorine products, hence it was decided to use it, with slight modifications, to compare the germicidal efficiencies of hypochlorites and quaternary ammonium compounds.

In the previous studies with chlorine compounds, the F.D.A. 209 strain of *Staphylococcus aureus* was selected as the principal test organism, since it had been found (18) to be much more resistant to chlorine compounds than Gram-negative organisms such as members of the coliform group. However, in view of the reported specificity displayed by surface-active agents (24) other bacteria of interest to the food industry were included in the present studies.

The importance of testing germicides in the concentrations at which they will be employed has been pointed out (19, 26). This has been borne in mind in the present studies. In addition, the period of contact with the germicide is of considerable practical importance. While in the sanitizing of vats, pipelines, coolers, etc., a contact period of several minutes can generally be allowed, in other instances, as in the treatment of farm dairy utensils, egg breaking sets, etc., the contact period often varies from an instantaneous dip to perhaps 10 sec. With this in mind, attention has been concentrated upon the ability of the products under test to bring about effective bacterial destruction within 1, 5, 10, or 20 sec.

Experimental

A 20 to 24 hr. growth of the F.D.A. strain of *S. aureus* on nutrient agar was washed off and suspended in sterile distilled water. After filtration through a No. 1 Whatman paper to remove clumps of organisms, the suspension was standardized to give a plate count of approximately 200,000,000 per ml. One millilitre of suspension was then introduced into 60 ml. of a 1 : 10 dilution of sterile skim-milk. The container for the inoculated skim-milk was of such dimensions that the depth of the liquid was 1½ in.

A previously sterilized slide was taken with sterile slide forceps and dipped into the seeded skim-milk suspension so that the lower half of the slide—an area of 1 by 1½ in. on either side—was immersed. The slide was withdrawn, carefully drained against the rim of the container for approximately 10 sec. to remove surplus liquid, then placed on end on a pad of sterile filter paper in a specially constructed draining can. A sufficient number of slides to run the desired number of tests on a given dilution of a product– usually four or five—were prepared consecutively, following which the tests were carried out before the films of diluted skim-milk had dried over more than 25% of the area. (Tests with slides allowed to dry completely give a significantly different picture.)

Previous to preparing the slides, 100 ml. portions of the solutions to be tested were placed in 100 ml. beakers and brought to the desired temperature. The slide first treated was then drained of any excess liquid on the filter paper layers in the draining can, dipped into the test solution, and gently agitated for the required period. At the end of the period it was quickly removed, dipped momentarily in a beaker of tap water (to minimize bacteriostatic action by the adhering germicide), shaken once to remove excess liquid, placed in a Petri dish, and the plate immediately poured with tryptone glucose agar containing 7.5% sodium chloride to inhibit contaminants (3, 22). Plates were counted after incubation at 37° C. for 48 hr. The remaining slides were similarly treated in correct sequence.

To obtain some idea of the number of organisms present on the slides before treatment with the germicide, control plates were prepared at regular intervals during each day's run by dipping sterile slides into a second container of diluted skim-milk in which the concentration of test organisms was only 1/60 to 1/600 of that of the original suspension. These slides were drained in the usual manner, then dipped in tap water before plating. The average colony count on these control slides, multiplied by the appropriate factor, reflected the approximate number of organisms present on the regular slides before treatment. By dividing this figure by 1000, a value was obtained indicating the number of organisms remaining after 99.9% had been destroyed. This was taken as the end-point in comparing the efficiency of the various products. Although the experimental error is obviously large when dealing with short exposure periods, the end-points obtained have shown far better agreement between replicate runs than has been obtained with various modifications of the F.D.A. method of determining the phenol coefficient.

The products tested were selected as being fairly representative of those on the market in Canada, and included:

(*a*) Roccal, a 10% solution of alkyldimethylbenzylammonium chloride.

(*b*) R-2-L, ditto.

(*c*) Hyamine 1622, (diisobutylphenoxyethoxyethyl)dimethylbenzylammonium chloride in crystalline form.

(*d*) Emulsept, a 10% solution of *N* (acylcolaminoformylmethyl) pyridinium chloride.

(*e*) Dalglish Liquid Bleach, a liquid sodium hypochlorite product containing about 12% available chlorine.

(*f*) Klenzade X4, a newer liquid sodium hypochlorite, said to be buffered to lower the pH and to render it more stable.

Results

SERIES I. *S. aureus*

To conserve space in presenting data, the average time required to reach the end-point (99.9% destruction) has been calculated for each dilution of each product. Table I shows that Roccal, R-2-L, and Hyamine 1622 possessed similar germicidal speed; Emulsept, on the other hand, was somewhat slower.

Although the Dalglish hypochlorite showed poorer agreement between the results of the two runs than did the remaining products, it appeared to be intermediate between Emulsept and the other three quaternary ammonium compounds. Klenzade X4, the second hypochlorite, was the slowest acting

TABLE I

EXPOSURE PERIODS (SECONDS) REQUIRED TO DESTROY 99.9% OF *S. aureus* AT 20° AND 45° C.

Compound	Concentration of active ingredient, p.p.m.			
	400	200	100	50
20° C.—(average of two runs)				
Roccal		5 (6.83)	5 (7.02)	10 (7.22)
R-2-L		5 (6.95)	5 (6.81)	10 (6.5)
Hyamine 1622		5 (6.48)	5 (6.88)	10 (7.02)
Emulsept		15 (5.32)	15 (6.85)	20 (7.02)
Dalglish	7.5 (10.8)	12.5 (10.48)	15 (9.98)	
Klenzade X4	>20 (11.02)	>20 (10.76)	>20 (10.2)	
45° C.				
Roccal		1	5	5
R-2-L		1	5	5
Hyamine 1622		1	5	5
Emulsept		10	5	10
Dalglish	1	1	5	
Klenzade X4	1	5	10	

N.B. Figures in parentheses represent pH values at 20° C.

of all, the end-point (99.9% destruction) not being reached within 20 sec. in either run.

To determine whether the residual germicide on the treated slide exerted a bacteriostatic influence, an additional slide was prepared for the five second exposure with the tap-water rinse omitted. Since there was close agreement between the counts on both rinsed and unrinsed slides, it was concluded that the bacteriostasis was insignificant. Nevertheless, the dip rinse was continued as a safeguard. (In subsequent tests with spores, using higher concentrations of quaternary compounds, the value of this step became more evident.)

The Influence of pH upon Germicidal Speed

It is well known that the germicidal speed of hypochlorites is reduced as the alkalinity increases (4, 15, 19, 30, 32). It has also been reported that the reverse holds true for cationic agents such as the quaternary compounds (2, 10, 13). Consequently, to determine whether differences in germicidal speed could be attributed to differences in reaction, the pH values for the various solutions were determined, using a Beckman pH meter. With the hypochlorites no attempt has been made to correct the readings for the alkaline salt errors (7); the actual differences between the two products are probably greater than those suggested by these readings.

The results (Table I) suggest that the superiority of Dalglish over Klenzade X4 was due to the lower alkalinity of the former. The more acid reaction of Emulsept at 200 p.p.m. might explain its slower action, but this would not apply in the 100 and 50 p.p.m. concentrations. To assess more directly the influence of pH, a second series of tests was conducted in which representative products were run at two different pH levels. These levels were obtained by substituting one-quarter strength buffer solutions of pH 6 and 10 (prepared from tablets manufactured by the Coleman Electric Co.*) for distilled water in preparing working dilutions of representative products. The results, together with the pH values obtained on the solutions immediately following the germicidal tests, appear in Table II.

TABLE II

GERMICIDAL POTENCY OF VARIOUS SANITIZING AGENTS AGAINST *S. aureus*, AT 20° C. AS INFLUENCED BY pH

Product	Conc., p.p.m.	Buffer solution pH	Actual pH	Period of exposure, sec., required for 99.9% destruction
Roccal	200	6	6.24	5
	100		6.20	5
	100	10	9.86	5
	50		9.90	20
	25		9.90	20
Emulsept	200	6	6.20	20
	100		6.19	20
	100	10	9.90	10
	50		9.90	20
	25		9.90	40
Klenzade X4	100	6	7.26	1
	50		6.82	1
	25		6.48	5
	400	10	10.49	5
	200		10.15	5
	100		9.98	40

While adjustment to a more alkaline level had little or no effect on the germicidal speed of Roccal and Emulsept, that obtained from the adjustment of Klenzade X4 to a less alkaline reaction was quite striking. Here a 25 p.p.m. concentration prepared from a pH 6 buffer solution showed fewer surviving organisms after a one second exposure than did 400 p.p.m. prepared from a pH 10 buffer solution. Comparisons with the results in Table I also show the greater activity of Klenzade X4 solutions prepared from the pH 10 buffer solution compared with those prepared without any adjustment of pH.

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* *The pH 6 buffer was composed of potassium acid phthalate and sodium phosphate; the pH 10 buffer of sodium tetraborate and sodium carbonate.*

At both pH levels Emulsept killed more slowly than Roccal, suggesting that the difference noted must be due to some factor other than the hydrogen ion concentration.

The Influence of Temperature Upon the Germicidal Speed

With hypochlorites, germicidal efficiency is significantly increased as the temperature of the solution is raised (4, 5, 18, 30, 32). In the sanitizing of egg breaking equipment, as well as of larger items of equipment in the food and dairy industries, it is frequently feasible to use warm or hot solutions of germicide. To determine the effect of higher temperatures in increasing the activity of both quaternary ammonium and hypochlorite solutions, a further series of tests was conducted at 45° C., this being the highest temperature found to be borne comfortably by the workers' hands.

The results (lower half of Table I) show a slight but distinct increase in germicidal speed of quaternary ammonium compounds when their temperature was raised from 20° to 45° C. This increase, however, was insignificant compared with that shown by the two hypochlorite products; with them, the germicidal efficiency was strikingly enhanced, so that 100 p.p.m. at 45° C. was considerably more effective than 400 p.p.m. at 20° C.

SERIES II. *Micrococcus candidus*

In view of current interest in thermoduric bacteria in market milk, a culture of a micrococcus (later identified as *M. candidus*) that had resisted laboratory pasteurization was obtained from Mr. A. Moldavan of the Guaranteed Pure Milk Company, Montreal. Using standard agar (1) four sets of tests were run with this organism at 20° C., the average of the results from three of which appear in Table III.

In the first set, the hypochlorites appeared to have a slight advantage in speed. However, when the second run was made some four weeks later, they appeared distinctly slower. Two further runs were made, in each of which the results favoured the quaternary compounds. No reason for this discrepancy could be discovered.

A single run was made at 45° C. The results (Table III) again indicate that higher temperatures enhance the efficiency of hypochlorites to a much greater extent than they do that of the quaternary compounds.

SERIES III. *Bacillus panis*

Since considerable importance is attached to the presence of spore-forming organisms in certain branches of the food industry, a strain of *B. panis*, isolated from ropy bread, was included in these studies.

In the first set of tests, to obtain spore forms the growth on 10-day-old cultures was washed off, standardized, rapidly heated to boiling in a water-bath to destroy vegetative forms, and again cooled before being used. In the second set, where vegetative organisms only were desired, poured plates received a surface inoculation from material picked from the margins of day-old colonies; the plates were incubated at 32° C. for 17 hr., the growth suspended, and standardized. After preparing the skim-milk dilutions for the test run, the remainder of the suspension was momentarily heated to boiling. Subsequent plating showed it to have contained approximately three spores per million vegetative cells.

TABLE III

EXPOSURE PERIODS (SECONDS) REQUIRED TO DESTROY 99.9% OF *M. candidus*, AT 20° AND 45° C.

Compound	Concentration of active ingredient, p.p.m.		
	200	100	50
20° C. (average of three runs)			
Roccal	5	5	10
R-2-L	5	5	10
Hyamine 1622	5	5	13
Emulsept	7	10	20
Dalglish	>20	>20	>20
Klenzade X4	>20	>20	>20
45° C.			
Roccal	5	5	5
R-2-L	5	5	5
Hyamine 1622	5	5	5
Emulsept	5	10	10
Dalglish	5	5	5
Klenzade X4	5	10	10

Owing to the spreading nature of the colonies, counting of plates was rather difficult. In an endeavour to improve the situation in the test run with the vegetative cells, the agar content of the medium (1) was raised to 2.5%. While this proved helpful, counting was still more difficult than with the other organisms studied.

The results of the two tests with spore suspensions of *B. panis* (Table IV) suggest that three of the quaternary ammonium compounds were decidedly more effective against spores than were the hypochlorites. However, the more favourable showing of the quaternary ammonium compounds may be partly due to the inhibitory influence of the higher concentrations of germicide adhering to the slide even after the slide had received a dip rinse. This will be discussed in a later section.

The single test carried out against the vegetative cells of *B. panis* (Table IV) revealed an entirely different picture. Here the superiority shown by the quaternary compounds against the spore forms is no longer evident. Both hypochlorites showed far greater activity against the vegetative cells than against the spores.

TABLE IV

EXPOSURE PERIODS (SECONDS) REQUIRED TO DESTROY 99.9% OF SPORES AND OF VEGETATIVE CELLS OF *B. panis*, AT 20° C

Compound	Concentration of active ingredient, p.p.m.				
	1000	400	200	100	50
Spores (average of two runs)					
Roccal	3	15	>20		
R-2-L	1	10	>20		
Hyamine 1622	1	>20	>20		
Emulsept	15	>20	>20		
Dalglish	>20	>20	>20		
Klenzade X4	>20	>20	>20		
Vegetative cells					
Roccal			5	5	5
R-2-L			5	>20	20
Hyamine 1622			1	5	5
Emulsept			5	5	10
Dalglish		1	1	5	
Klenzade X4		5	5	5	

SERIES IV. *Lactic Acid Streptococci*

The importance of the lactic acid streptococci in the dairying industry suggested the desirability of including them in these studies. To this end, a cheese starter (No. 43) currently in use at the Central Experimental Farm Dairy was selected. This starter comprises a variety of strains of lactic acid streptococci and aroma-producing organisms, and is fairly representative of the types of organisms that might be encountered in shipping cans in which whey had been returned from the factory. In order to preserve the quantitative relation between the various strains in the starter, it was deemed best to use a milk culture of starter, incubated at 21° C. for 22 hr., to inoculate the skim-milk diluent, rather than culturing on laboratory media and standardizing the suspension in the usual manner. On the basis of preliminary trials, the starter was diluted with sterile skim-milk to give a plate count of approximately 200,000,000 per ml. Since the majority of the organisms formed chains of varying length, the number of cells present was actually far in excess of that indicated by the plate count. Plates were poured with Bacto whey agar with the addition of 1.0% yeast extract, and incubated at 32° C. for 72 hr.

The results from the first run showed a surprising lack of resistance to both types of germicide. For the second run, therefore, the concentrations of germicides were cut in half. Although all six products were very effective, the hypochlorites had some advantage at all three concentrations tested (Table V).

SERIES V. *Escherichia coli*

In view of the widespread use of the coliform test as a check on the adequacy of sanitizing procedure in milk pasteurization plants, studies with this organism seemed particularly appropriate. Difco Violet Red Bile Agar was used as the plating medium, and counts were made after 20 hr. incubation at 37° C.

TABLE V

EXPOSURE PERIODS (SECONDS) REQUIRED TO DESTROY 99.9% OF CHEESE STARTER ORGANISMS AT 20° C. (AVERAGE OF TWO RUNS)

Compound	Concentration of active ingredient, p.p.m.		
	100	50	25
Roccal	5	5	10
R-2-L	3	5	10
Hyamine 1622	3	8	20
Emulsept	3	8	10
Dalglish	1	1	5
Klenzade X4	1	5	5

The data in Table VI indicate that the quaternary ammonium compounds were less effective here than they were against *S. aureus*. This is in contrast to the hypochlorites, which are generally most active against Gram-negative organisms (15, 16, 19).

TABLE VI

EXPOSURE PERIODS (SECONDS) REQUIRED TO DESTROY 99.9% OF *E. coli*, AT 20° AND 45° C.

Compound	Concentration of active ingredient, p.p.m.				
	400	200	100	50	25
20° C (average of two runs)					
Roccal		15	20	>20	
R-2-L		10	>20	>20	
Hyamine 1622		>20	>20	>20	
Emulsept		15	>20	>20	
Dalglish	1	1	3		
Klenzade X4	1	1	3		
45° C.					
Roccal			5	5	>20
R-2-L			5	10	10
Hyamine 1622			5	20	>20
Emulsept			5	10	>20
Dalglish			1	1	5
Klenzade X4			1	5	5

The Influence of pH upon Germicidal Speed

As with *S. aureus*, a series of tests was carried out on representative products diluted to working concentration with buffer solutions. The results (Table VII) again showed only a very slight stepping-up of potency of the quaternary compounds through the upward adjustment of pH. The activity of the hypochlorite (Klenzade X4) was greater at a lower pH value, but the effect was less than that noted with *S. aureus* (Table I).

TABLE VII

GERMICIDAL POTENCY OF VARIOUS SANITIZING AGENTS AGAINST *E. coli* AT 20° C. AS INFLUENCED BY pH

Product	Concentration, p.p.m.	Buffer solution pH	Actual pH	Period of exposure (sec.) required for 99.9% destruction
Roccal	200	6	6.18	10
	100		6.11	20
	100	10	9.25	10
	50		10.00	>20
R-2-L	200	6	6.35	10
	100		6.35	20
	100	10	10.25	10
	50		10.25	20
Emulsept	200	6	6.00	>20
	100		6.01	>20
	100	10	9.96	20
	50		9.99	>20
Klenzade X4	50	6	6.72	1
	25		6.40	5
	10		6.25	5
	200	10	10.30	1
	100		10.11	1
	50		10.01	5

N.B. 99.9% destruction leaves 27 colonies.

The Influence of Temperature on Germicidal Speed

A single run made at 45° C. (Table VI) showed a slightly greater increase in effectiveness of the quaternary compounds than was noted with *S. aureus.* These compounds were, however, invariably much less effective than were the hypochlorites at the higher temperature, although the acceleration of germicidal speed of the hypochlorites was less marked than with *S. aureus.*

SERIES VI. *Pseudomonas aeruginosa*

In view of the marked resistance displayed by this organism toward various antibiotics, it was included as one of the test organisms. Plates were poured with tryptone glucose skim-milk agar (1) and incubated at 20° to 25° C. for 48 hr.

The data in Table VIII indicate that *P. aeruginosa* showed slightly less resistance than *E. coli* to the quaternary ammonium compounds, but somewhat more to the hypochlorites. Against both organisms the hypochlorites were the more effective sterilizing agents.

TABLE VIII

EXPOSURE PERIODS (SECONDS) REQUIRED TO DESTROY 99.9% OF *P. aeruginosa*, AT 20° C.

(Average of two runs)

Compound	Concentration of active ingredient, p.p.m.			
	400	200	100	50
Roccal		5	10	>20
R-2-L		5	15	>20
Hyamine 1622		7.5	>20	>20
Emulsept		7.5	10	20
Dalglish	1	1	5	
Klenzade X4	1	5	5	

BACTERIOSTATIC ACTION OF QUATERNARY COMPOUNDS

When these studies were nearing completion, our attention was directed to the recent report by Klarmann and Wright (21). In a modification of the F.D.A. technique for determining the phenol coefficient of quaternary ammonium compounds, these workers used sterile glass strips 10 by 38 mm., which were placed in the 'medication tubes'. After 10 min. exposure of the test organism, the glass strip was withdrawn and plated. Where the glass strip had been immersed in a 333 p.p.m. solution of a quaternary compound, a definite area of inhibition of growth of *S. aureus* could be seen (Fig. 3 in their paper). This led us to re-examine our data to discover whether such bacteriostatic action might be influencing our results.

In the tests with spores of *B. panis*, it was noted that on the plates poured on slides treated with 1000 and 400 p.p.m. solutions of the quaternary compounds, no colonies appeared on or adjacent to the slide itself, while with the hypochlorites, the majority of the colonies were on or near the slide. A similar paucity of colonies on the slide itself where the higher concentrations of quaternary compounds were used had been noted earlier with *S. aureus*. (This effect is illustrated by Fig. 1, in which Roccal and Dalglish are compared against *M. candidus*.) The plates from slides treated with 200 p.p.m. of the quaternary compounds showed some colonies on or near the slides.

That definite bacteriostasis was occurring with the higher concentrations of the quaternary compounds was confirmed by various methods, including the plating of sterile slides dipped directly into the quaternary solution, then subjected to rinsing treatments varying from a quick dip to 20 sec. in length. The plates were poured with agar medium heavily seeded with the test organism. These tests showed some growth inhibition with all three Gram-positive organisms tested (*S. aureus*, *B. panis*, and *M. candidus*) while the Gram-negative organisms (*E. coli* and *P. aeruginosa*) failed to show any such effect. The results from the most comprehensive series of tests are shown in Table IX. The control (unrinsed) slides showed marked inhibition of growth with concentrations of Roccal from 1000 to 100 p.p.m. inclusive; with the dip rinse, this was confined to the 1000 and 400 p.p.m. concentrations, while with the 20 sec. rinse the inhibition was almost negligible. In Sections *D*, *E*, and *F*, an anionic compound, Fisher's Laboratory Aerosol, at 10 p.p.m. was substituted for tap water, the intention being to neutralize the effect of the cationic quaternary compound adhering to the slide. The results, however, show little evidence of such neutralization. Similar results were obtained in another set of tests in which another anionic compound, Nacconal FSNO, was also included.

TABLE IX

DEGREE OF INHIBITION BY ROCCAL. SEEDED CULTURE *S. aureus*

Treatment of slide (sterile) after dipping in Roccal	Roccal, p.p.m.				
	1000	400	200	100	50
	Degree of inhibition (++++—complete)				
A. Dip rinse, tap water	++++	+++	+	+	O
B. 5 sec. rinse, tap water	+	Slight	+	Very slight	Very slight
C. 20 sec. rinse, tap water	Very slight	Very slight	Slight	O	O
D. Dip rinse; Aerosol, 10 p.p.m.	++++	++	+	+	Slight
E. 5 sec. rinse; Aerosol, 10 p.p.m.	<+	+	Very slight	<+	Very slight
F. 20 sec. rinse; Aerosol, 10 p.p.m.	<+	<+	Slight	+	Very slight
G. No rinse, control	++++	++++	++	++	Slight

To determine whether the clear zones represented inhibition or actual killing, a bent needle was touched to areas where growth was abundant, then to clear areas. After overnight incubation at 37° C., the inoculated areas were again touched with the bent needle and transfers made to oval tube slants of tryptone glucose agar (28). These were again observed for growth after overnight incubation. Of 155 'fishings', 97 showed no growth on subculturing; where growth did occur; the site of the original 'spotting' was approaching the area of visible growth. As a further check, the bent needle was touched directly to the medium in the clear zones, then to oval tube slants. Growth took place in only 19 of 117 such 'fishings'. It would appear, therefore, that in addition to inhibition, there is actual killing of bacteria by the small amount of quaternary compound carried over on the slide. While this complicates the precise evaluation of the germicidal efficiency of these compounds in the higher concentrations, from the practical standpoint it must be regarded as a distinct advantage, particularly where the period of contact with the germicide is short, as in the case of farm sanitization of dairy utensils.

An unexpected phenomenon was encountered when the tests reported in Table IX were repeated, substituting slides previously dipped in sterile diluted skim-milk for plain slides. It was expected that the film of organic matter would tend to lower both bactericidal and bacteriostatic effectiveness of the quaternary compounds. Instead, the zones of inhibition were appreciably larger than those where plain slides were used (Fig. 2). This may be due to greater adsorption and retention of Roccal by the film of milk solids. Further studies on this phase are being carried out.

The bulk of our studies on bacteriostasis were carried out with Roccal. However, the other three quaternary products have all shown a similar effect in varying degree, as illustrated in Fig. 3, where *M. candidus* was the test organism. Here are shown plates of slides that received a one-second treatment with each of the four quaternary compounds in concentrations of 200 and 100 p.p.m. respectively. Each slide received a momentary dip in tap water before being placed in the Petri dish. The order of decreasing bacteriostasis, Roccal >R-2-L>Hyamine 1622>Emulsept, has been noted in several of the regular experimental runs, the first two being definitely more inhibitory than the last two. Neither of the two hypochlorites showed any sign of bacteriostasis in concentrations up to 1000 p.p.m.

Discussion

With the exception of the plant studies reported by Scales and Kemp (32), Jamieson and Chen (14), and Krug and Marshall (23), most attempts to evaluate the germicidal efficiency of surface-active compounds have been by means of the F.D.A. technique for the determination of the phenol coefficient, or some modification thereof. The difficulty of obtaining consistent results with the F.D.A. technique in the testing of chlorine compounds (19) has been similarly reported for quaternary ammonium compounds by various workers (21, 29, 34). Aside from this, major objections to the phenol coefficient technique are that (*a*) it only indicates complete destruction of the test organisms,

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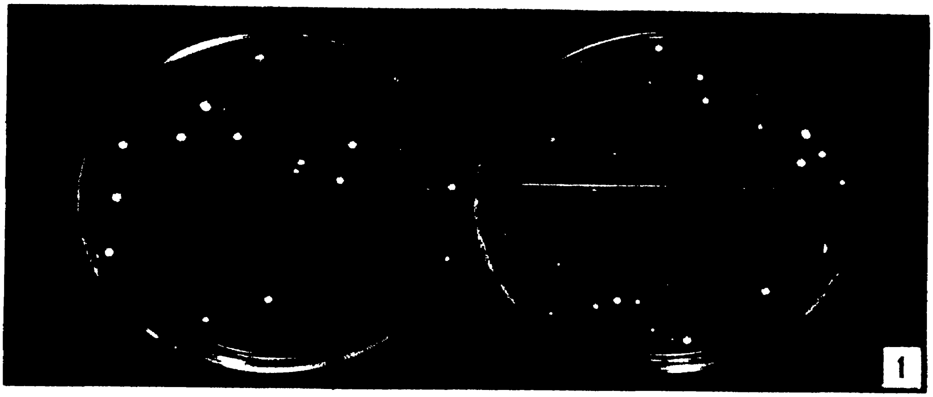
FIG. 1. *Illustrating relative scarcity of colonies on or near slide treated with Roccal 100 p.p.m for five seconds (left-hand side), compared with one treated with Dalglish 200 p.p.m. 20 sec. (right-hand side). (M. candidus, test organism.)*

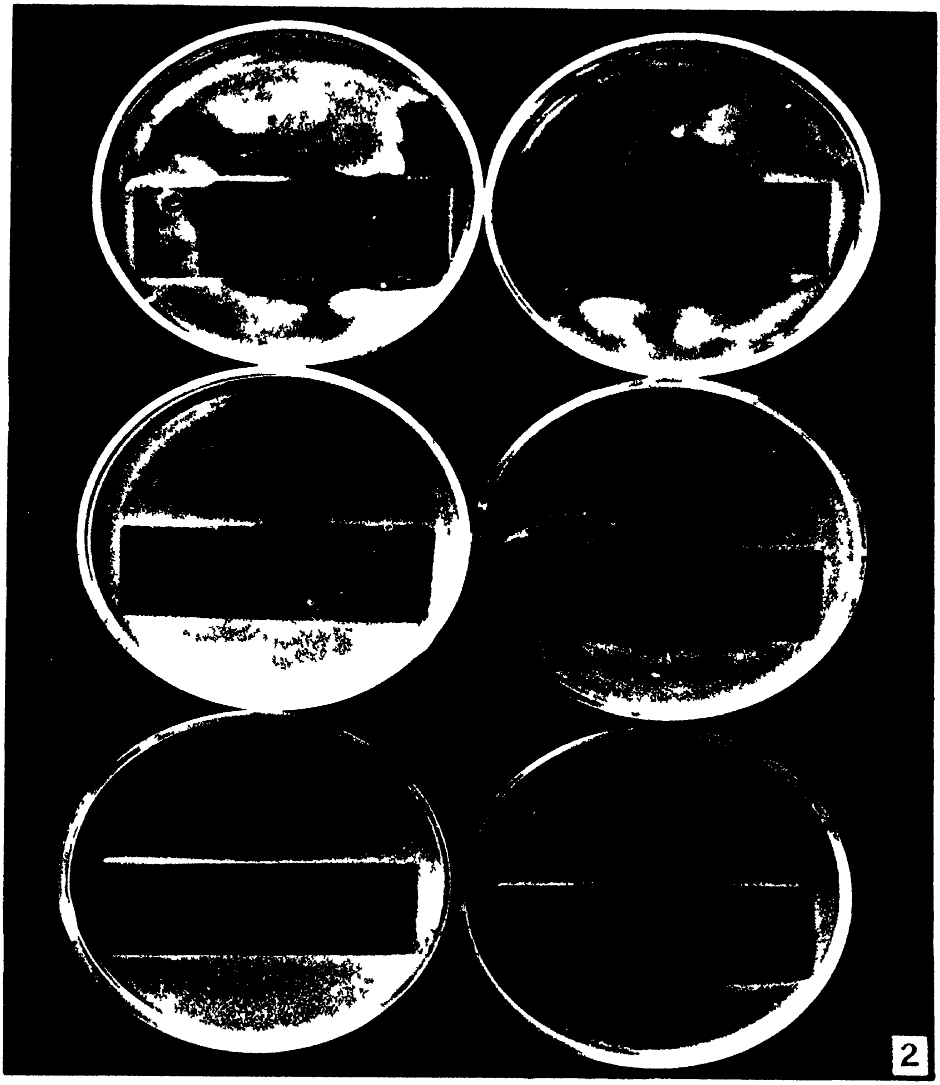
FIG. 2. *Illustrating inhibitory effect of Roccal 100 p.p.m. carried over on glass slide (S. aureus, test organism). Top pair, no rinse after treatment; centre pair, dip rinse; bottom pair, five second rinse. Plain slides on left-hand side; slides dipped in sterile 10% skim-milk on right-hand side.*

FIG. 3. *Comparative bacteriostatic effect of four quaternary compounds. One second exposure, M. candidus. (A) Roccal, (B) R-2-L, (C) Hyamine 1622, (D) Emulsept. Left-hand side = 100 p.p.m. Right-hand side = 200 p.p.m.*

Plate I

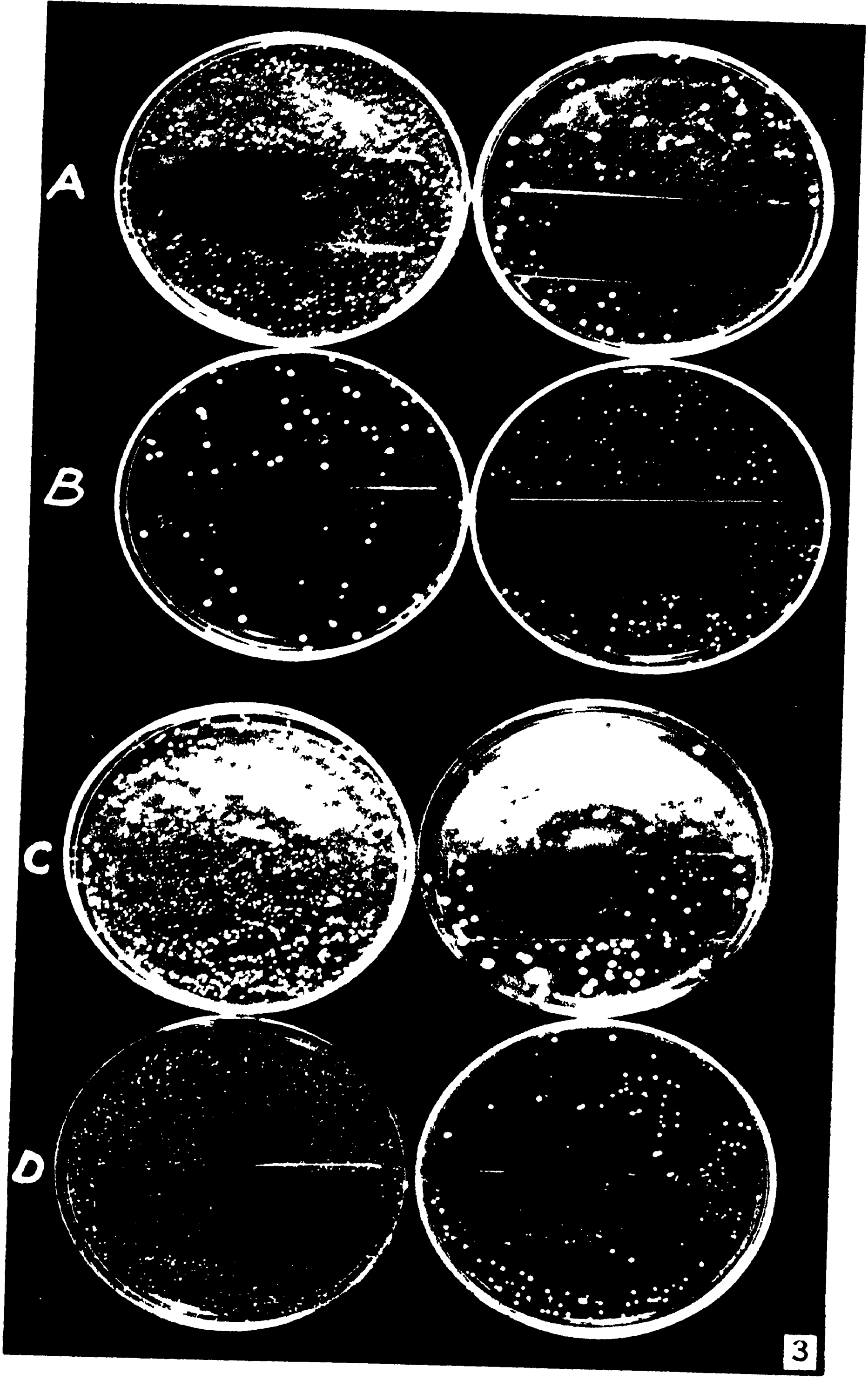


1



2

PLATE II



telling nothing about the proportion of the organisms surviving after shorter periods of exposure; (*b*) it measures the killing effect of germicides where the test organisms are freely suspended in the solution of germicide, rather than in a film on a surface; and (*c*) it is based upon the determination of the concentration of germicide required to give complete killing in 10 min., but not in 5, rather than the measurement of the effectiveness of the germicide in the concentrations used in practice (19, 26). It was largely to avoid these objections that the glass slide technique was devised. In this technique, the organisms are present in a partially dried film of skim-milk, thus simulating conditions encountered in the sanitizing of food handling utensils and equipment. The proportion of skim-milk is of course far in excess of that that would be encountered on well washed equipment, but occasionally slip-ups do occur, and it is well to have the test method cover the most extreme conditions likely to be encountered.

In addition to approximating more closely the conditions under which bacteria have to be destroyed in plant sanitizing procedures, the glass slide method has other advantages. It possesses great flexibility in that the temperature, period of exposure, test organism, plating medium, concentration of germicide, etc., may all be varied to suit the requirements of the investigator. As to reproducibility of results, far less variability can be expected than with tests of the phenol coefficient type. A final point is that through gentle agitation of the slide during the period of contact with the germicide, any superiority of detergent action of a given product has an opportunity to exert itself, and, by mechanical removal of the film and its accompanying bacteria, reduce the number of organisms remaining on the slide.

The bacteriostatic influence of the small quantity of quaternary compound carried over on the slide after rinsing in tap water is not believed to have influenced the comparisons between these products and hypochlorites significantly. While with strong solutions the effect is quite evident on a crowded plate, with the usual concentrations it is practically unnoticeable when the number of colonies approaches the 99.9% end-point. From a practical standpoint, this continuing effect may be regarded as an advantage, as sterilization of metal surfaces of utensils and equipment would continue for some time in the residual film of solution. In view of the findings of Valko and DuBois (35) and others, the failure of attempts to neutralize this bacteriostatic action by rinsing in solutions of anionic compounds was surprising. Possibly orientation of the adsorbed molecules of quaternary compounds leaves the actively germicidal groups in contact with the milk film, so that the anionic molecules cannot react with them.

These studies indicate that it is unsafe to generalize concerning the relative values of quaternary compounds and hypochlorites in the sanitizing of food plant equipment. Much depends upon the type of organism most likely to be prevalent. As was shown to be the case with chlorine sterilizing agents (19, 20), some quaternary products are more effective than others. An important point in plant operations is that hypochlorites respond much more readily to favourable adjustments of pH and temperature than do the quaternary compounds tested.

Despite their greater stability, non-corrosiveness and other desirable features, their higher cost makes it unlikely that quaternary compounds will immediately replace hypochlorites in most phases of plant sanitation. There are, however, certain special fields in which they may excel. One is in the sanitizing of egg breaking sets; the emollient effect of the quaternary solution contrasts with the irritating effect of hypochlorites on the skin, hence breakers or kitchen help are much less averse to putting their hands into the sanitizing solution when treating washed breaking sets. There is the further point that certain of these quaternary compounds leave on the hands a resistant invisible film that retains bacteria beneath it (27). Another is in the treatment of milk shipping cans; whether cans are washed by hand or by machine, a small percentage of a suitable quaternary compound in the final rinse would help prevent growth of bacteria in remaining traces of moisture, while reducing the corrosion that generally follows the use of the more active hypochlorites for such a purpose. Similarly, in the treatment of beverage glasses, dishes, and silverware, the quaternary compounds leave less odour and are easier on the skin, while their lower sensitivity to added organic matter maintains the germicidal potency longer than is the case with hypochlorites.

The greater effectiveness of the quaternary compounds against spores of *B. panis* is of interest in that Scales and Kemp (33) reported that Roccal was ineffective against spores of *B. subtilis*. On the other hand, Green and Birkeland (11) found cetylpyridinium chloride effective against spores of *B. subtilis* and other aerobic and anaerobic species, and Heineman (12) reported destruction of spores of *B. subtilis* in less than five minutes by 2,000 p.p.m. of Roccal. The ineffectiveness of the chlorine compounds is in line with previous findings (15).

Acknowledgments

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THE EFFECT OF WEATHERING ON VARIOUS ROTPROOFING TREATMENTS APPLIED TO COTTON TENTAGE DUCK[1]

By C. H. Bayley[2] and Muriel W. Weatherburn[2]

Abstract

Cotton tentage duck treated with ferric oxide–chromic oxide ('mineral khaki'), copper carbonate–ferric oxide ('copper–iron'), cuprammonium, cutch–cuprammonium, copper 8-quinolinate, copper glyoxime, 2,2'-dihydroxy-5,5'-dichlorodiphenylmethane, zinc dimethyldithiocarbamate, copper naphthenate, copper hydroxynaphthenate, zinc naphthenate, and mercuric naphthenate, showed varying degrees of breaking strength loss when subjected to outdoor weathering during the summer months. The losses were in no case greater than that of the untreated fabric, and certain treatments, such as mineral khaki and cutch–cuprammonium, gave considerable protection against loss in breaking strength. With copper naphthenate, copper hydroxynaphthenate, and mercuric naphthenate the degree of chemical degradation as measured by cuprammonium fluidity was somewhat greater than that of the untreated fabric. The presence of a waterproofing treatment consisting of a mixture of petroleum-base waxes in addition to the rotproofing treatments usually resulted in increased breaking strength loss. The water resistance of the waxed samples showed a slight to pronounced increase on weathering. In general there was considerable loss of rotproofer as a result of weathering; with the copper compounds this loss was of the order of 37 to 90%, but was reduced to 6 to 44% by the presence of wax. Weathering produced an almost complete loss of the two zinc compounds, 2,2'-dihydroxy-5,5'-dichlorodiphenylmethane, and mercuric naphthenate. Losses of metal from chromium–iron proofings were negligible even in the absence of wax proofing. The degree of rot resistance as judged by soil burial was greatest in the fabrics treated with copper, and was increased by the presence of wax. The water resistance of samples subjected to soil burial was frequently decreased before the occurrence of any marked loss in breaking strength; this indicates microbiological attack on the wax coating prior to attack on the cotton fabric.

The weathering characteristics of chemical substances used for the purpose of imparting resistance to microbiological attack in cotton textiles for outdoor use are of considerable importance. In addition to the obvious disadvantages of those compounds possessing an appreciable solubility in water or poor stability to sunlight, it is undesirable for the compound to catalyze the actinic degradation of the fabric.

It has been reported that impregnation of cotton fabrics with certain compounds such as chromic oxide (9, 10, 16) or certain copper–tannin complexes (1) results in increased resistance to actinic degradation. Hayes (13) states that the fastness to light and weather conditions of the chromic oxide–ferric oxide treatment known as 'mineral khaki' was not excelled by any other treatment. The action of waterproofing waxes on the chemical degradation of cotton yarns (14) and canvas (15) has been studied by Jarrell and Holman, who found that the presence of such waxes in cotton yarns subjected to weathering did not result in increased actinic degradation while with cotton duck, especially where 'yellow petrolatum' was used, there was a marked increase in the extent

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[2] *Chemist.*

of degradation. Jarrell and Holman attribute these differences to the greater degree of heating to which the cotton duck was exposed during the weathering process. The degradation was markedly reduced by the inclusion of pigments with the wax. It has been shown that the presence of copper soaps used as rotproofers in concentrations up to 1% copper did not materially increase the extent of actinic breakdown occurring in cotton tarpaulin duck (4) and in various types of cordage fibres (3). It was also found (4) that the presence of a wax-pigment-filler type of compound in conjunction with the copper rotproofer resulted in decreased breaking strength and metal losses on weathering.

In the present study the weathering characteristics of a number of rotproofers applied to cotton tentage duck, with and without waterproofing wax, have been studied. The extent of the degradation produced by weathering was judged by the extent of breaking strength loss and increase in cuprammonium fluidity, while the loss in rotproofing efficacy was determined by means of the standard soil burial technique. Measurements of changes in water resistance and loss of rotproofer resulting from weathering were also carried out.

Materials Used

The fabric used was an unbleached cotton army duck weighing 10 oz. per sq. yd. and having 46 three-ply yarns per inch in the warp and 37 two-ply yarns per inch in the weft. With the exception of the 8-hydroxyquinoline and dimethylglyoxime, all the chemicals used were of technical (commercial) grade.

Details of Treatments

The concentrations of treating compounds applied to the fabric were chosen on the basis of previous experience or of recommendations received from other investigators. With few exceptions, as indicated, the treatments were applied in the laboratory, mostly by aqueous procedures. With copper, zinc, and mercuric naphthenates, the treatments were applied from solution in Stoddard solvent (dry cleaners' naphtha) as previously described (2). The copper naphthenate treated fabric was of a pale blue-green colour, the others colourless.

A number of 12 in. (warpwise) by 18 in. (weftwise) specimens were cut from a single bolt of fabric and, of these, four were selected at random for each treatment. Two of these specimens were subjected to weathering, the other two being tested as indicated below without previous weathering. The two weathered specimens were each subdivided into four subspecimens, each of which was sufficient to provide five 1-in. wide ravelled warp strips for breaking strength determinations. Breaking strength determinations were run on the first subspecimen from each of the two weathered specimens (two replicates of five breaks each), on the second pair of subspecimens after burial for two weeks, on the third after burial for four weeks, the fourth subspecimen being held in reserve. The two unweathered specimens were also divided into four subspecimens as above, and breaking strength determinations carried out on the first subspecimen from each of the two specimens after leaching (original breaking strength), on the second pair of subspecimens after burial for two weeks without leaching, on the third after leaching and burial for two weeks, and on the fourth after leaching and burial for four weeks.

In the aqueous treatments the four 12 in. by 18 in. specimens for each treatment were sewn together along the 12 in. edge to form a strip, passed through the motor-driven rubber-covered rolls of a laboratory padder, which could be operated at a speed of 20 ft. per min., and the free ends of the strip connected through a 'runner' of fabric to form a continuous loop approximately 6 ft. in circumference. The runner was passed beneath a brass roll and the latter lowered into the treating solution (10 litres) contained in an enamelled pan that could be heated when necessary, and the loop of fabric run through the bath. At the conclusion of the treatment, unless otherwise indicated, the fabric was washed for two hours in running tap water and dried at room temperature. In all the aqueous treatments the loop of fabric was previously wetted out by passage through a solution of a wetting agent (a 0.1% solution of technical sodium lauryl sulphate in the form of Gardinol WA was used).

A duplicate series of treated samples was also prepared containing a waterproofing wax coating consisting of a mixture of paraffin wax* and petrolatum No. 2** having the following characteristics:

—	Parowax	Petrolatum No. 2
Melting point, ASTM, °F.	122 - 125	114 - 120
Say. visc. at 210° F., sec.	33 - 38	64 - 71
Penetration at 77° F., cone	—	170 - 220
Colour	+25+ Say. (water white)	35Y 70R 2 in. cell
Oil content, %	0 5 max.	About 35

The paraffin wax and petrolatum were used in a ratio of 3 : 1 by weight, and were applied subsequent to the rotproofing treatment from a Stoddard solvent bath having a concentration calculated to give approximately 10% of wax on the weight of the fabric. When the rotproofer was applied from solution in Stoddard solvent, the wax was incorporated in the solution containing the rotproofer.

The details of the aqueous treatments are given below. The weight of chemicals shown refers to the amount added to 10 litres of distilled water; the temperatures of the treatments and the length of time during which the loop of fabric was run through the treating bath are also shown.

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* *'Parowax' (refined paraffin wax), Imperial Oil Ltd.*

** *'Petrolatum No. 2' Imperial Oil Co.*

(1) Chromium–iron ('Mineral Khaki')

Bath (1)—1200 gm. chromic sulphate ($Cr_2(SO_4)_3 \cdot 5H_2O$) plus 500 gm. ferrous sulphate at 70° C. for 15 min.

Bath (2)—500 gm. sodium hydroxide at room temperature for 30 sec.

Colour of treated fabric—medium tan.

In addition to the sample treated as above, a sample of commercially processed chromium–iron ('mineral khaki') proofed tentage duck* was included in this series. In view of the fact that chromium–iron treated fabrics are known to show poor rot resistance when exposed to conditions of heavy contamination, e.g., soil contact, it was thought desirable to investigate the characteristics of a chromium–iron sample aftertreated with copper naphthenate, a substance that is known to have good resistance to possible deterioration resulting from soil contact. Samples of the commercially processed fabric were therefore treated with copper naphthenate applied from a solvent bath as previously described (2).

(2) Copper–iron

This treatment, involving the impregnation of the fabric with a mixture of copper and iron salts followed by passage through a solution of sodium carbonate, is based on the finding of Race and co-workers at the University of Leeds (19). The concentrations of the treating solutions were adjusted to give metal contents on the treated fabric of 0.5 to 1.0% copper oxide and 0.7 to 1.25% ferric oxide.

Bath (1)—930 gm. ferric ammonium sulphate ($Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$) plus 990 gm. copper sulphate ($CuSO_4 \cdot 5H_2O$) at 70° C. for 15 min.

Bath (2)—500 gm. sodium carbonate (anhydrous) at 50° C. for 10 min.

Colour of treated fabric—orange tan.

(3) Cutch–cuprammonium

The cutch (quebracho) extract used in this treatment was in solid form.

Bath (1)—200 gm. cutch dispersed in 5 litres of water and added to 100 gm. of copper sulphate dissolved in 5 litres of water; run at 70° C. for 20 min.

Bath (2)—100 gm. sodium dichromate at 50° C. for 15 min.

Bath (3)—500 gm. copper sulphate, dissolved in water and ammonium hydroxide added until the precipitate was just dissolved; run at room temperature for 15 min.

Colour of treated fabric—chocolate brown.

(4) Copper Hydroxynaphthenate

A stock solution of 200 gm. Nuodite Copper 25%† in 250 gm. ammonium hydroxide (28% NH_3) was diluted with water to give the desired copper content on the fabric, and the fabric run through the solution for 20 min. at room temperature.

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* *Obtained from the Chief Inspector of Stores, Central Ordnance Depot, Didcot, Berks., England.*

† *Obtained from Nuodex Products of Canada Ltd., Leaside (Toronto), Ont.*

Colour of treated fabric - a pale blue-green somewhat lighter than that of copper naphthenate.

(5) Copper 8-Quinolinate

This treatment was based on recommendations received from the Monsanto Chemical Co. (12).

Bath (1)- 625 gm. glacial acetic acid mixed with 312 gm. 8-hydroxyquinoline and the mixture added to 10 litres of water. Run at 82° to 88° C. for 15 min.

Bath (2)—200 gm. copper acetate ($Cu(C_2H_3O_2)_2H_2O$) at room temperature for 10 min.

Colour of treated fabric- greenish yellow.

(6) Copper Glyoxime

The procedure was a modification of the method of Neish and co-workers (17).

Bath (1) - 100 gm. dimethylglyoxime at 98° C. for 10 min.

Bath (2)—100 gm. copper acetate at room temperature for 30 min.

Colour of treated fabric—yellow green.

(7) 2,2'-Dihydroxy-5,5'-dichlorodiphenylmethane

A commercial preparation of this compound in the form of the product G-4* was applied from solution in sodium hydroxide and the free base precipitated in the fabric by treatment with acetic acid.

Bath (1)—160 gm. G-4 and 28.8 gm. sodium hydroxide at room temperature for 15 min.

Bath (2)—500 gm. glacial acetic acid at room temperature for 15 min. For the treatment at the lower concentration, Bath (1) was diluted 1 : 1 with distilled water. Owing to the alkalinity of the Ottawa tap water the rinsing of the treated fabric was carried out in distilled water.

Colour of treated fabric— unchanged.

(8) Zinc Dimethyldithiocarbamate

In applying this treatment the fabric was impregnated with a solution of commercial sodium dimethyldithiocarbamate** and the zinc compound precipitated by passage through a solution of zinc sulphate.

Bath (1)—200 gm. sodium dimethyldithiocarbamate solution (stated by the manufacturer to have a nitrogen content of 3.29% corresponding to approximately 30% active ingredient) at room temperature for 15 min.

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* *Obtained from Givaudan Delawanna Inc., 330 W. 42nd Street, New York.*

** *Obtained from Naugatuck Chemicals, Elmira, Ont.*

Bath (2)—100 gm. zinc sulphate at room temperature for 10 min. For the treatment at lower concentration, Bath (1) was diluted 1 : 1 with distilled water.

Colour of treated fabric—unchanged.

(9) Cuprammonium

This was a commercially proofed sample*, medium green in colour.

Methods

The fabrics were weathered on the eastern end of the roof of the National Research Laboratories, Sussex Street, Ottawa, from May 31, 1945, to Sept. 30, 1945. The samples were fixed to wooden racks that were set at an angle of 45° facing southwest, care being taken on the one hand to avoid attaching the samples to the frames under tension, and on the other to avoid a degree of looseness such as would permit undue flapping of the samples in the wind. The distance from the roof to the lower edge of the samples was 2½ ft. A record of maximum and minimum temperatures during the exposure period was kept by means of a thermometer attached to one of the racks.

Rot resistance was determined by the soil burial method (7), tests being run on the original, weathered, and leached samples. Leaching was carried out in 1 litre bottles through which tap water at 25° C. flowed at a rate of 10 litres per hour, the duration of leaching being 24 hr. Breaking strength measurements were made by the ravelled strip method on specimens ravelled to 1 in. and conditioned at 70° ± 5° F. and 65% relative humidity ± 2%. Water resistance was measured by the variable head method (6). Cuprammonium fluidity measurements were carried out on conditioned samples using the method of Clibbens and Little (8). The portions of the waxed samples used for fluidity determinations were previously freed of wax by extraction with Stoddard solvent. Copper analyses were made by the ignition method (5). The preliminary phases of the chromium and iron determinations were made by Method 35 C of the analytical methods recommended by the Textile Institute of Great Britain (21), the chromium determinations being completed by Method 37 (*a*) and the iron determinations by the method of Race (18). In the latter method the iron in the hydrochloric acid solution was reduced by the addition of a few drops of stannous chloride solution (3% solution in 3 *N* hydrochloric acid). The solution was cooled, 2 ml. saturated mercuric chloride solution was added to destroy excess stannous chloride, and the solution titrated immediately with *N*/10 potassium dichromate using barium diphenylamine *p*-sulphonate as indicator. Copper and iron when present together were determined by the method of Race (18) with a slight modification of the procedure for copper—i.e., to the ammoniacal filtrate acetic acid was added in slight excess and the solution titrated with thiosulphate as in the method for copper alone (5).

* *Obtained from the Willesden Proofing Co. Inc., New York, N.Y., U.S.A.*

Zinc in fabrics treated with zinc naphthenate was determined by the hydrolysis method (26), the acid solution being titrated with ferrous ammonium sulphate (25). Zinc dimethyldithiocarbamate was determined by the colorimetric method (22) involving conversion to the copper compound, mercury by the method of Shiraeff (20), and 2,2′-dihydroxy-5,5′-dichlorodiphenylmethane by the method of Gottlieb and Marsh (11). Determinations of the pH of the untreated fabric were made according to the method of Wakeham and Skau (24).

Data

(1) Weather Conditions

From the weather data in Table I it will be noted that conditions were favourable to actinic degradation. Comparison of weather conditions with those of the previous summer (4) shows that the average total hours of sunshine per month were similar but that the rainfall in the present series was markedly greater (4.19 in. per month compared with 2.57 in.). There was some evidence of superficial growth of a species of the fungus *Alternaria* on the underside of the untreated fabric.

TABLE I

WEATHER CONDITIONS DURING EXPOSURE OF SAMPLES

Period	Mean daily temperature, °F.		Rainfall, in.	Bright sunshine, total hours
	Maximum	Minimum		
May 31 – June 3	56	37	0	35.9
June 4 – June 10	66	43	1.00	52.0
June 11 – June 17	82	59	1.17	48.7
June 18 – June 24	79	57	0.32	55.3
June 25 – July 1	90	59	0.64	67.7
July 2 – July 8	86	62	0.10	76.4
July 9 – July 15	78	56	2.29	38.1
July 16 – July 22	82	58	0.21	63.3
July 23 – July 29	90	66	0.13	64.3
July 30 – Aug. 5	89	61	1.10	59.6
Aug. 6 – Aug. 12	93	58	0.47	57.3
Aug. 13 – Aug. 19	87	59	0.50	54.6
Aug. 20 – Aug. 26	89	56	1.91	51.2
Aug. 27 – Sept. 2	82	58	1.13	40.8
Sept. 3 – Sept. 9	94	64	0.07	58.5
Sept. 10 – Sept. 16	84	56	0.79	39.2
Sept. 17 – Sept. 23	62	45	3.20	28.4
Sept. 24 – Sept. 30	68	47	1.73	29.0
Average	81	56		
Total			16.76	920.3

(2) Breaking Strength Loss

Breaking strength data are given in Table II. The breaking strength losses of treatments that were applied to fabric cut from the same bolt were subjected to statistical analysis. It became apparent that the effects of the various treatments were significantly different in both the waxed and unwaxed samples

TABLE II

EFFECT OF WEATHERING AND BURIAL ON LOSS OF BREAKING STRENGTH

Treatment	Original breaking strength, lb.	Breaking strength loss, %					
		Weathered	Buried 2 weeks	Leached buried 2 weeks	Weathered buried 2 weeks	Leached buried 4 weeks	Weathered buried 4 weeks
Not waxed							
Untreated	175	41.7	97.8	100.0	89.0	100.0	100.0
Chromium–iron	163	8.6	88.4	94.5	90.8	100.0	100.0
*Chromium–iron	150	22.0	64.0	83.3	93.3	100.0	—
*Chromium–iron aftertreated with copper naphthenate	152	11.2	Zero	11.2	20.4	24.3	—
Copper–iron	204	45.6	4.9	2.5	55.7	8.8	94.5
*Cuprammonium	139	38.9	+7.2	+11.5	50.0	+18.0	54.8
Cutch–cuprammonium	175	17.7	5.2	2.9	38.2	1.7	25.6
Copper naphthenate	174	40.3	4.0	12.6	64.4	39.1	100.0
Copper hydroxynaphthenate	161	33.0	+4.4	0.6	62.1	57.8	100.0
Copper 8-quinolinate	197	33.0	+0.5	1.0	43.3	23.4	47.3
Copper glyoxime	162	27.2	+9.9	6.8	47.6	1.2	88.9
Zinc dimethyldithiocarbamate (*A*)	169	43.8	+3.0	12.4	86.3	93.0	100.0
Zinc dimethyldithiocarbamate (*B*)	161	37.2	+4.4	+7.5	86.3	34.2	100.0
Zinc naphthenate	177	38.4	19.8	27.1	82.7	92.7	100.0
Mercury naphthenate	158	41.2	100.0	100.0	78.5	100.0	100.0
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*A*)	157	38.2	+10.2	67.5	83.4	100.0	100.0
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*B*)	164	45.1	+9.7	56.7	71.9	100.0	100.0
Waxed							
Untreated	188	70.8	99.5	96.9	88.2	100.0	—
Chromium–iron	191	34.5	67.5	62.9	82.1	100.0	100.0
*Chromium–iron	163	28.2	25.2	23.9	57.0	100.0	100.0
*Chromium–iron aftertreated with copper naphthenate	163	22.1	1.2	3.7	23.9	7.4	41.7
Copper–iron	193	36.8	5.7	20.2	38.0	14.0	41.0
*Cuprammonium	167	62.4	+3.6	0.6	56.4	0.6	61.5
Cutch–cuprammonium	191	27.2	+0.5	1.5	31.1	14.7	31.1
Copper naphthenate	184	57.1	9.8	5.4	62.5	13.6	59.2
Copper hydroxynaphthenate	189	55.0	16.4	16.4	57.2	41.8	58.3
Copper 8-quinolinate	192	30.7	2.1	1.0	34.9	6.3	34.9
Copper glyoxime	192	53.2	21.4	16.7	54.7	24.5	57.2
Zinc dimethyldithiocarbamate (*A*)	196	66.9	17.9	19.9	85.7	91.4	100.0
Zinc dimethyldithiocarbamate (*B*)	194	67.5	17.0	21.6	79.8	46.4	100.0
Zinc naphthenate	187	69.5	11.2	19.8	82.9	82.4	100.0
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*A*)	184	65.8	3.3	28.2	79.3	82.6	100.0
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*B*)	185	68.6	+8.1	0.5	75.1	15.1	100.0

* *Commercially treated.*

under all conditions of weathering and burial. The necessary difference between sample averages of breaking strength loss (10 breaks) for significance at the 5% level is approximately 12% for all treatments involving soil burial, and approximately 6% for those involving weathering.

(a) Weathering Effects

The colour of the chromium–iron treated fabric was not changed by weathering, all of the other coloured fabrics unwaxed showing some fading. The copper–iron and cutch–cuprammonium treatments retained considerable brown coloration but the upper surface of the other copper treated fabrics was colourless.

The untreated fabric showed a substantial breaking strength loss and this was more pronounced in the presence of wax. The unwaxed samples treated with chromium–iron, cutch–cuprammonium, copper hydroxynaphthenate, copper 8-quinolinate, and copper glyoxime treatments showed lower breaking strength losses than the untreated fabric. The waxed samples, with the same treatments and, in addition, copper–iron, cuprammonium, and copper naphthenate, were superior to the waxed untreated sample. In general the breaking strength losses of the waxed samples were greater than those of the unwaxed, the only exceptions being the commercial chromium–iron, copper–iron, and copper 8-quinolinate treated samples. With the unwaxed and waxed commercially treated chromium–iron samples aftertreated with copper naphthenate, it will be noted that the presence of the copper naphthenate did not increase the breaking strength loss above that shown by the samples containing chromium–iron alone.

(b) Burial Effects

Unwaxed treatments that were completely resistant to soil burial for four weeks with preliminary leaching were the copper–iron, cuprammonium, cutch–cuprammonium, and copper glyoxime. Treatments that withstood burial for two weeks but gave moderate losses after four weeks were chromium–iron + copper naphthenate, copper naphthenate, copper hydroxynaphthenate, copper 8-quinolinate, and zinc dimethyldithiocarbamate (0.49%). 2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane was resistant to burial for two weeks without leaching, but with preliminary leaching the breaking strength losses were substantially increased. Zinc naphthenate suffered moderate breakdown on two-week burial and almost complete breakdown after four weeks. The chromium–iron and mercury naphthenate treated fabrics showed little resistance to soil burial but the commercial chromium–iron fabric aftertreated with copper naphthenate was resistant. The addition of wax frequently caused a substantial reduction in the breaking strength loss as for example in samples containing 2,2′-dihydroxy-5,5′-dichlorodiphenylmethane when leached and buried for two and four weeks.

The losses in breaking strength of all samples subjected to soil burial after weathering were substantial although when allowance is made for the losses produced by weathering alone the effect attributable to soil burial is not excessive in most cases. Thus in the unwaxed fabrics, burial for four weeks after weathering produced no additional loss in strength with the cutch–cuprammonium, and barely significant losses with the cuprammonium and copper 8-quinolinate treated samples. All other unwaxed treated samples showed almost complete breakdown when buried for four weeks after weathering, although burial for two weeks after weathering produced no loss in strength additional to that shown on weathering alone with the chromium–iron treatment with a copper naphthenate aftertreatment and copper–iron treated samples, and caused only 20 to 30% loss in strength in the copper glyoxime, copper naphthenate, and copper hydroxynaphthenate treated samples. In the case of the unwaxed samples, with the exception of the chromium–iron aftertreated with copper naphthenate, none of the copper treatments showed significant increases in breaking strength loss as a result of four weeks' burial after weathering, all the other waxed treatments showing complete breakdown.

(3) Loss of Treating Compound

Data for the loss of the treating compounds as a result of weathering are given in Table III. With the treatments containing chromium and iron, it had

TABLE III

LOSS OF TREATING COMPOUND ON WEATHERING

Treatment	Analysis	Not waxed			Waxed		
		Concentration, %		Loss on weathering, % of orig.	Concentration, %		Loss on weathering, % of orig.
		Orig.	Weath.		Orig.	Weath.	
Chromium–iron	Cr Fe	1.28 0.70	1.26 0.60	1.5 14.3	1.14 0.60	1.20 0.68	+ 5.3 +13.3
*Chromium–iron	Cr Fe	0.80 0.77	0.85 0.64	+ 6.2 18.6	0.75 0.76	0.85 0.58	+13.3 23.7
*Chromium–iron aftertreated with copper naphthenate	Cr Fe Cu	0.75 0.77 0.19	0.79 0.70 0.12	+ 5.3 9.1 36.8	0.82 0.76 0.16	0.77 0.78 0.14	6.1 + 2.6 12.5
Copper–iron	Cu Fe	0.65 0.70	0.07 0.66	89.1 5.7	0.50 0.70	0.54 0.78	+ 8.0 +11.4
*Cuprammonium	Cu	1.41	0.72	49.0	1.40	1.11	20.7
Cutch–cuprammonium	Cu	1.85	0.53	71.5	1.46	1.21	17.1
Copper naphthenate	Cu	0.33	0.08	75.7	0.31	0.18	41.9
Copper hydroxynaphthenate	Cu	0.34	0.07	70.6	0.34	0.22	35.3
Copper 8-quinolinate	Cu	0.80	0.15	81.3	0.72	0.68	5.6
Copper glyoxime	Cu	0.49	0.10	79.6	0.48	0.27	43.8
Zinc dimethyldithiocarbamate (*A*)	Total compound	0.29	0.00	100.0	0.20	0.02	90.0
Zinc dimethyldithiocarbamate (*B*)	Total compound	0.49	0.04	91.9	0.45	0.05	88.8
Zinc naphthenate	Zn	0.79	0.00	100.0	0.88	0.00	100.0
Mercury naphthenate	Hg	0.01	0.00	100.0	—	—	—
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*A*)	Total compound	0.55	0.02	96.3	0.48	0.01	98.0
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*B*)	Total compound	1.00	0.13	87.0	0.91	0.07	91.2

* *Commercially treated.*

been noted that the distribution of these elements in the treated fabric was not as uniform as would have been expected, and this undoubtedly accounts for the apparent increase in the content of these elements noted in some of the weathered samples. The data are sufficient to indicate that there is no substantial loss of either chromium or iron during weathering. The copper concentration of all copper treatments was reduced substantially by weathering. In the unwaxed treatments there was less copper lost from the chromium–iron aftertreated with copper naphthenate treatment than from any of the other copper treatments. This effect is being studied further. The presence of wax reduced the loss of copper, there being practically no loss from the waxed copper–iron and copper 8-quinolinate treatments, and only moderate losses with the other copper treatments. In the latter group the percentage loss of copper from the cuprammonium and cutch–cuprammonium treatments was lower than that from copper naphthenate, copper hydroxynaphthenate, and copper glyoxime. It should, however, be borne in mind that these original concentrations of copper in the cuprammonium and cutch–cuprammonium treatments were higher than in the other copper treatments. The other treating compounds, namely zinc dimethyldithiocarbamate, zinc naphthenate, mercury naphthenate, and 2,2′-dihydroxy-5,5′-dichlorodiphenylmethane were removed either completely or almost completely by weathering.

(4) Water Resistance

Comparison of the laboratory samples to which wax was applied from a solution in Stoddard solvent in a separate operation after the rotproofing treatment shows that the original water resistance of the treated fabrics was somewhat higher than that of the untreated fabric containing wax alone (Table IV), although, on weathering, the water resistance of the untreated waxed sample was increased. For all treatments except the chromium–iron, in which the water resistance decreased slightly on weathering, the water resistance was increased on weathering. For samples that had been leached and buried for four weeks the water resistance of the cuprammonium, copper 8-quinolinate, and 2,2′-dihydroxy-5,5′-dichlorodiphenylmethane (0.91%) was approximately the same as, or greater than, the original value, the resistance of the other treatments being substantially reduced.

(5) Cuprammonium Fluidity

The cuprammonium fluidity data are given in Table V. It is apparent that the fluidity of the original cutch-cuprammonium treated fabric is slightly higher than that of the untreated fabric. In all other laboratory treatments there is no evidence of chemical damage resulting from the treating procedures. Although it was not possible to measure the fluidity of the untreated fabric from which the commercially treated chromium–iron sample had been prepared, the fluidity of the commercial chromium–iron samples appears considerably higher than that usually obtained with an unbleached cotton duck, and it is therefore reasonable to conclude that some chemical damage had occurred in the commercial processing of this sample. On weathering,

TABLE IV

EFFECT OF WEATHERING AND BURIAL ON WATER RESISTANCE OF WAXED FABRICS

Treatment	Water resistance, cm. pressure to cause leakage			Change in water resistance, % of original	
	Orig.	Weath.	Leached and buried four weeks	Weathered	Leached and buried four weeks
Untreated	29	44	0	+52	−100
Chromium–iron	55	51	0	− 7	−100
*Chromium–iron	35	—	0	—	−100
*Chromium–iron aftertreated with copper naphthenate	38	33	19	−13	− 50
Copper–iron	45	53	20	+18	− 56
*Cuprammonium	40	49	54	+23	+ 35
Cutch–cuprammonium	50	55	17	+10	− 66
Copper naphthenate	32	47	21	+47	− 34
Copper hydroxynaphthenate	47	51	18	+ 9	− 62
Copper 8-quinolinate	50	55	52	+10	+ 4
Copper glyoxime	44	49	12	+11	− 73
Zinc dimethyldithiocarbamate (*A*)	39	47	9	+21	− 77
Zinc dimethyldithiocarbamate (*B*)	40	44	—	+10	—
Zinc naphthenate	27	41	13	+52	− 52
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*A*)	35	54	14	+54	− 60
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*B*)	35	52	40	+49	+ 14

* *Commercially treated.*

the untreated fabric showed a considerable increase in fluidity, the effect being slightly more pronounced in the waxed fabric. With the unwaxed samples the rise in fluidity was markedly less than that of the untreated fabric for the chromium–iron and copper 8-quinolinate treatments. With the waxed samples the copper–iron, cutch-cuprammonium, and copper glyoxime treatments were also effective in reducing chemical degradation. Copper naphthenate, with and without wax, and copper hydroxynaphthenate and mercury naphthenate, unwaxed, showed increases in cuprammonium fluidity somewhat greater than that shown by the untreated fabric.

Discussion of Data

Attention is called to the appreciable amount of degradation on weathering which took place in the waxed samples as compared with the unwaxed samples. It was thought that the wax coating might have caused the adherence to the fabric of particles of acidic dirt from the air, and consequently a comparison of the pH of the waxed and unwaxed fabrics after weathering might be of value (Table VI). It will be noted that the pH values for waxed and unwaxed fabrics are similar and, although the decrease in pH value as the result of

TABLE V

EFFECT OF WEATHERING ON CUPRAMMONIUM FLUIDITY

Treatment	Cuprammonium fluidity, reciprocal poises					
	Not waxed			Waxed		
	Orig.	Weath.	Increase on weathering	Orig.	Weath.	Increase on weathering
Untreated	3.3	16.8	13.5	3.9	20.6	16.7
Chromium–iron	3.1	7.3	4.2	3.2	6.1	2.9
*Chromium–iron	8.3	16.6	8.3	7.2	15.5	8.3
*Chromium–iron aftertreated with copper naphthenate	9.9	14.2	4.3	9.5	15.0	5.5
Copper–iron	2.8	14.7	11.9	4.0	8.0	4.0
*Cuprammonium	4.5	17.2	12.7	4.7	18.0	13.3
Cutch–cuprammonium	5.8	19.1	13.3	5.9	16.7	10.8
Copper naphthenate	2.5	21.7	19.2	2.4	21.7	19.3
Copper hydroxynaphthenate	2.7	20.6	17.9	3.1	18.4	15.3
Copper 8-quinolinate	2.4	12.3	9.9	3.3	10.8	7.5
Copper glyoxime	2.4	17.3	14.9	3.3	12.6	9.3
Zinc dimethyldithiocarbamate (*A*)	2.5	16.3	13.8	3.9	20.7	16.8
Zinc dimethyldithiocarbamate (*B*)	2.5	14.4	11.9	3.3	19.8	16.5
Zinc naphthenate	3.0	17.0	14.0	3.3	19.9	16.6
Mercury naphthenate	2.8	21.1	18.3	—	—	—
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*A*)	2.8	15.2	12.4	3.7	19.7	16.0
2,2′-Dihydroxy-5,5′-dichlorodiphenylmethane (*B*)	2.8	15.7	12.9	2.2	19.6	17.4

* *Commercially treated.*

TABLE VI

pH OF UNTREATED FABRIC

Sample	pH	
	Original	Weathered
Untreated, not waxed	6.2	5.9
Untreated, waxed	6.7	5.6

weathering is greatest for the waxed fabric, it is not considered that the final value for the pH of the latter fabric is indicative of the possibility of damage through acid attack. The damage must therefore be attributed to oxidative changes intensified by the presence of the wax compound, and this effect is being studied further.* Mention has already been made of the findings of Jarrell and Holman (15) with regard to the deteriorating effect of yellow petrolatum on cotton canvas. These authors found that the addition of pigments decreased the deteriorating effect. It is therefore possible that in previous work in this laboratory on the weathering of cotton duck (4) the inclusion of iron oxide pigment in the wax compound prevented any accelerated damage that might have been caused by the wax.

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* *Indications are that the increased degradation is attributable to a great extent, if not entirely, to the petrolatum.*

In general the breaking strength losses on burial of the waxed samples were less than those of the unwaxed and also the loss of treating compound on weathering was less marked. However, in the waxed samples treated with zinc dimethyldithiocarbamate, zinc naphthenate, and 2,2′-dihydroxy-5,5′-dichlorodiphenylmethane the treating compound was almost completely removed on weathering, so that the behaviour with respect to soil burial after weathering was similar to that of the untreated fabric. It might be mentioned that the untreated fabric that had been weathered was slightly superior on burial to the original untreated fabric. This factor is in agreement with other observations that weathering retards subsequent attack by microorganisms (2, 4, 10, 16, 23).

With regard to the water resistance of the waxed fabrics after burial it may be noted that the treatments that showed no change in water resistance, namely cuprammonium, copper 8-quinolinate and 2-2′-dihydroxy-5,5′-dichlorodiphenylmethane (0.91%) also showed no appreciable change in breaking strength when leached and buried for four weeks. Fabrics containing other treatments that gave either no loss or slight loss in breaking strength when leached and buried for four weeks, namely chromium–iron aftertreated with copper naphthenate, copper–iron, cutch–cuprammonium, and copper naphthenate, showed substantial loss of water resistance. This would indicate that the water resistance is destroyed through microbiological attack on the wax before destruction of the cellulose takes place.

The data give additional evidence of the beneficial effect of the chromium–iron treatment in protecting against photochemical degradation, but also of the inability of this treatment to withstand exposure to conditions of severe contamination such as exist in the soil burial test. The addition of copper naphthenate to chromium–iron improved the rot resistance without affecting the resistance of the treated fabric to weathering. Race and Rowe (18) have reported that the addition of copper to chromium greatly diminishes or entirely destroys the protective value of chromium against weathering. The present data do not substantiate their findings. However, it should be pointed out that in their experiments the chromium oxide content was quite low, 0.39%, and also that the copper was in the form of the carbonate.

All copper compounds, without wax, showed considerable resistance to burial for two weeks even after preliminary weathering that had resulted in the removal of a large percentage of the copper. The cuprammonium, cutch–cuprammonium, and copper 8-quinolinate treatments were more satisfactory than the copper naphthenate, copper hydroxynaphthenate, and copper glyoxime, although it should be remembered that the copper concentrations of the former treatments were considerably higher than those of the latter before and after weathering. With wax, the copper compounds all gave good resistance to burial for four weeks even after weathering.

It should be noted that from breaking strength data there was no evidence of enhanced photochemical degradation in the copper treated samples; in fact, the cutch–cuprammonium treatment with a copper concentration of 1.85% gave considerable protection, especially with the unwaxed sample. It is possible that the dark brown colour produced by this treatment had an effect in decreasing the photochemical degradation.

The Problem of the Protection of Tentage Ducks

One of the reasons for undertaking the present investigation was to obtain information regarding the weathering characteristics of a number of the more promising rotproofing treatments such as may be applicable to cotton duck used in the manufacture of tentage for the Canadian Armed Services.

The climatic conditions under which tentage may be used will vary widely, and several types of environments can be listed (Table VII).

TABLE VII

CONDITIONS OF VARIOUS ENVIRONMENTS IN WHICH MICROBIOLOGICAL ATTACK IS POSSIBLE

Environment number	Climatic zone	Season	Temperature	Rainfall	Sunlight intensity	Probable intensity of microbiological attack*
1	Temperate (open country)	Summer	Moderate to high	Moderate	High	Low to moderate
2	Temperate (varying degrees of shade)	Summer	Moderate	Moderate	Moderate to high	Low to moderate
3	Tropics (open country)	All seasons	Moderate to high	Moderate to high	High	Moderate
4	Tropics (shade–jungle)	All seasons	Moderate to high	Moderate to high	Low to moderate	High

* *This refers to microbiological attack occurring in fabrics above ground level; under conditions of soil contamination, attack may be expected in all of the four environments.*

In addition to the environments given in Table VII reference should be made to the possibility of the occurrence of microbiological attack under conditions of storage. Experience has shown that cotton textiles in the temperate zone can readily undergo severe attack under conditions of humid storage at moderate to high temperatures in the spring, summer, and autumn seasons. Thus there are on record numerous cases in Canada of severe deterioration of untreated cotton textiles used in conjunction with service equipment (e.g., covers for army vehicles).

From a consideration of Table VII, it is reasonable to assume that provision should be made for the rotproofing of cotton tentage fabrics designed for use in environments Nos. 1 to 4, and, if such fabrics are liable to be used in *any* of these environments, the treatment chosen should be the one that provides the best resistance to microbiological attack and at the same time possesses good weathering characteristics with the minimum tendency to promote actinic degradation.

It has been shown in the present paper that the resistance to weathering of most of the rotproofers examined was markedly improved by a waxing treatment, but that the extent of actinic degradation is liable to be increased by the presence of wax. Moreover, it is sometimes argued that the loss in air permeability that results from waxing a tentage fabric is undesirable. For this reason there has been considerable interest in the range of so-called 'self-sealing' cotton canvases, recently developed by the British Cotton Industries Research Association, in which a high degree of water resistance, together with a normal level of air permeability, is obtained by a suitable choice of yarn twist factors and weaving densities. Hence, consideration may well be given to rotproofing treatments suitable for use on (*a*) ordinary tentage duck in which wax is used to increase the water resistance of the fabric, and (*b*) special ducks of the self-sealing type in which no wax treatment for the purpose of imparting water resistance is necessary.

In so far as requirement (*a*) is concerned, it is probable that a chromium–iron treatment aftertreated with copper naphthenate and wax, copper–iron waxed and copper 8-quinolinate waxed would be the most satisfactory. These treatments appear to exert a marked protective action against actinic degradation of the cotton while providing a high level of resistance to microbiological attack under conditions of severe contamination; the wax in such treatments provides a satisfactory level of water resistance and does not appear to enhance appreciably the actinic breakdown of the fabric. The losses of copper shown by these treatments on weathering were lower than those of any of the other copper compounds at the concentrations examined.

With respect to requirement (*b*) it is probable that the chromium–iron treatment aftertreated with approximately 3% copper naphthenate would be the most satisfactory. This treatment possesses all of the advantages cited for the three above-mentioned compounds except for the fact that the copper is removed to a marked degree by weathering. However, there should be no great difficulty in reapplying copper naphthenate to tentage in use. The copper–iron and copper 8-quinolinate treatments both showed severe loss of copper on weathering, and this loss could not be conveniently restored by re-treating in the field.

From time to time, objections have been raised to the use of copper naphthenate because of its characteristic odour. The odour of this compound varies between wide limits and it is believed that by the adequate specification of the properties of the naphthenic acids from which the compound is prepared, it should be possible to overcome this difficulty. The copper naphthenates used in this laboratory have not possessed highly objectionable odours, and when applied to fabrics in the concentrations used in the various investigations on rotproofing have imparted little or no odour to the treated fabric.

Some mention might be made of the suitability of a chromium-iron treatment alone for use under requirements (*a*) and (*b*). This treatment, in which the chromium is the constituent toxic to micro-organisms, has long been widely used in Great Britain and, provided not less than 0.75% of chromium (as Cr_2O_3) is present, is known to possess a moderate degree of rotproofing efficacy. This treatment would probably be adequate for exposures above ground level, under the conditions of environment No. 1. It has been shown that the accumulation on tents of decaying leaves has brought about the rotting of fabric treated with chromium-iron. For many years a chromium-iron treatment has been applied to tentage duck used by the Canadian Army, although the degree of rot resistance shown by the treated duck has been of a low order and there has been considerable deterioration of tentage pitched in open country in Canada, through microbiological attack during the summer months (see Fig. 1). It should be pointed out that the chromium oxide contents of the fabrics concerned were exceedingly low.

The problem of a colourless rotproofing treatment having the efficacy of the treatments discussed above still remains to be solved. None of the colourless compounds examined in the present investigation showed satisfactory resistance to weathering, even when present in conjunction with wax. Other colourless compounds that have been investigated as rotproofers include salicylanilide, phenolic compounds, and organo-mercurials. These compounds have not been found to possess high efficacy under conditions favouring severe microbiological attack, and most of them show unsatisfactory weathering characteristics. However, some of these compounds, notably salicylanilide, have been successfully used as preservatives for cotton textiles during storage.

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PLATE I

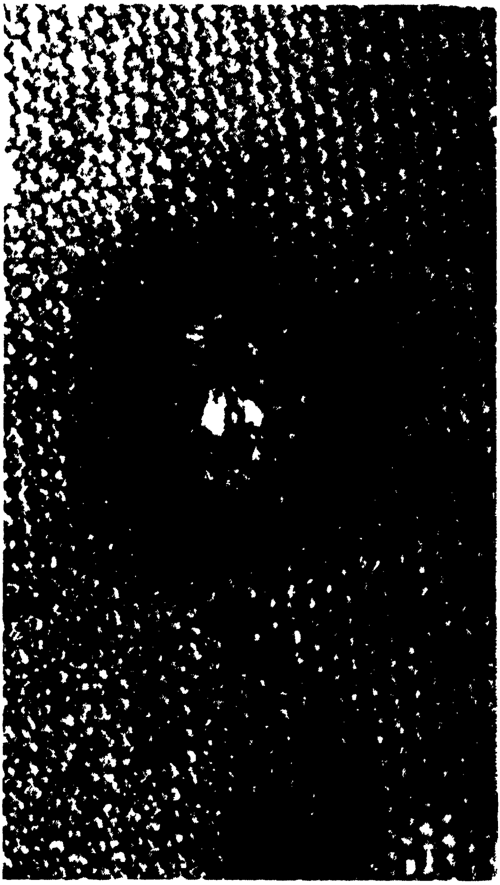

FIG. 1 *Army tent duck (12 oz.) taken from Canadian Army Tent Circular showing deterioration caused by microbiological attack occurring during use in Canada*

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HYGROSCOPIC EQUILIBRIA FOR HULLS AND KERNELS OF SUNFLOWERSEED AND OATS[1]

BY R. COLVIN,[2] B. M. CRAIG,[2] AND H. R. SALLANS[3]

Abstract

An apparatus for adjusting a stream of air to definite relative humidities using saturated salt solutions and the application of this equipment to the determination of hygroscopic moisture in grains is described. Data are presented to show that under equilibrium conditions sunflower hulls have a higher moisture content than meats. For oats this condition is reversed. In the lower humidity ranges sunflower and oat hulls show similar moisture contents, which fall about 2% below the values for wheat, oat groats, flax, and sunflower meats computed to an oil-free basis. It is concluded that hygroscopic equilibria in grains are governed more by the structure of the grain and physical absorption phenomena than by the chemical components.

In previous studies on sunflowerseed and oats (4, 7) differences in moisture level between hulls and meats were observed. This is not surprising, since a marked difference exists in the composition of these two parts of the seed. The hulls of both sunflowerseed and oats are composed mainly of cellulose, hemicelluloses, and lignin and should behave similarly, but the meats differ markedly from the hulls in their components and should show a difference in moisture absorption. Furthermore, since sunflower meats and oat groats differ greatly in composition, it would be expected that this difference would be reflected in their moisture holding capacity.

Since the moisture distribution between meats and hulls is related to the problem of dehulling (4), it appeared of practical interest to investigate this relation.

Methods and Materials

In a previous study (4) samples were exposed to constant relative humidities by supporting them over saturated salt solutions at a controlled temperature of 25° C. At high humidities it required two to three weeks for diffusion processes to establish equilibrium between the seed and the surrounding air. Under these conditions, difficulties were encountered due to mould growth on the samples (5).

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To hasten the establishment of equilibrium conditions the apparatus shown in Fig. 1 was devised. This consists of a prehumidifier, *A*, constructed from a milk bottle with a sintered glass disk in the inlet tube; a humidification tower, *B*; a spray trap, *C*; a sample tube, *D*; and a vacuum ballast fitted with a vacuum regulator. Final adjustment of humidity is accomplished in tower *B* by means of saturated salt solutions.

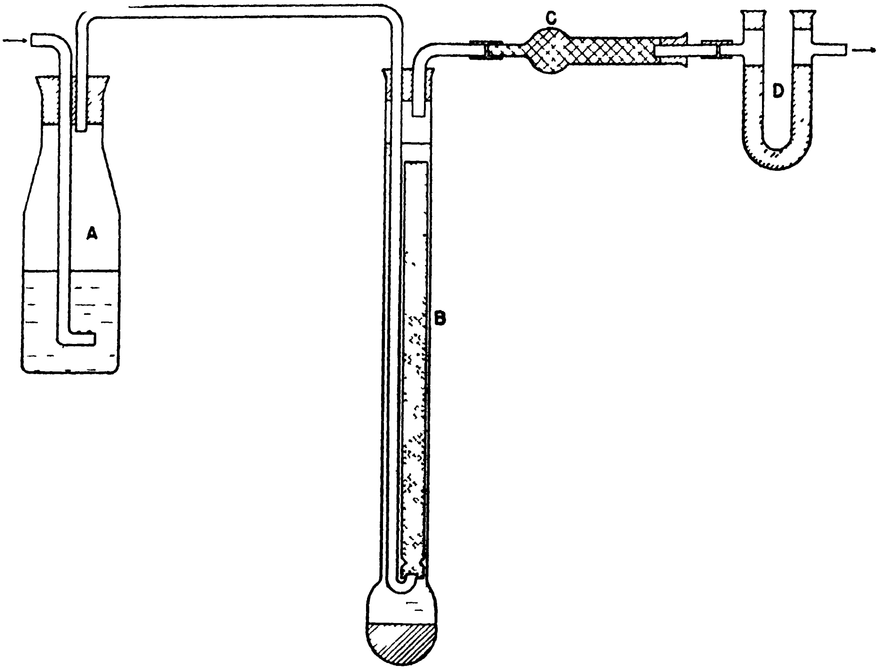

FIG. 1. *Apparatus for obtaining constant humidity in establishing hygroscopic equilibria.*

An inner tube filled with glass beads is supported in tower *B* by means of the air inlet tube. Some solid salt is placed in the bottom of *B*, which is then filled to the top of the inner tube with a saturated solution of the required salt. In operation, air aspirated through the bead column induces a circulation of the solution, which passes up through the bead column and down the outer jacket where it comes in contact with solid salt at the bottom of tower *B*. This action insures that the solution will always be saturated and that no supersaturation will occur owing to quiescent evaporation that might occur in a static system.

When air is fed directly to the humidifying tower, evaporation from the solution causes crystallization to occur in the inlet tubes with plugging of the system. To overcome this difficulty a prehumidifier was introduced and charged with a solution not quite saturated with respect to the salt being used in the tower. To obtain the higher humidities, 81% and 93%, pure water was used in the prehumidifiers since the normal room humidity was in the order of 30 to 40%.

A battery of five units was set up in a room thermostatically controlled at 25° ± 2° C. The units were all connected to a common vacuum ballast and air flow through each unit adjusted to 500 ml. per hr. by means of capillaries in the lines.

As a check on the effectiveness of humidity control, a volumetric hygrometer (1) was constructed and measurements were made of actual humidities obtained. The salts used, together with humidities as given in the International Critical Tables and experimentally determined values, are shown in Table I. The theoretical values and those actually produced by the equipment agree within the experimental error of the volumetric hygrometer.

TABLE I

RELATIVE HUMIDITIES OF SATURATED SALT SOLUTIONS AT 25° C.

Salt	Relative humidity, %	
	From Tables	Experimental
$CaCl_2 . 6H_2O$	31.0	31.0
K_2CO_3	43.0	43.0
$Ca(NO_3)_2$	51.0	50.0
NH_4NO_3	62.0	60.5
$NH_4Cl + KNO_3$	71.2	71.0
$(NH_4)_2SO_4$	81.1	80.0
$NH_4H_2PO_4$	93.0	91.5

A sample of the material under study was placed in the U-tube, *D*, which was then connected in the aspiration system. At intervals the tube was removed, the arms closed, and the tube weighed. When constant weight was obtained, usually after five to six days, the sample was removed and moisture determined in a vacuum oven at 100° C. with a 16 hr. heating period.

It requires several days before mould growth begins at high moisture levels and only in a very few cases at the highest humidity levels was there any evidence of moulding.

The sunflower samples used were of the Mennonite variety from experimental plots at the University of Saskatchewan. The seed was harvested at high moisture content (25 to 30%) and air-dried in the laboratory to a level of 4.5 to 5.0%. At this value the hull composed 45 to 50% and the meats 50 to 55% of the kernel weight.

Victory oats grown at the University of Saskatchewan were used for the study. The sample had a bushel weight of 45 lb. and was composed of 26.3% hulls and 73.7% groats.

Since it is obviously impossible to dehull seed at high moisture levels without loss of moisture, hygroscopic equilibria were determined on whole seed and on meats and hulls after separation. The sunflower seed was carefully hulled by hand for initial studies, but subsequent work indicated that hulls separated mechanically gave almost identical results if care was used to exclude all traces of meats. The oats were dehulled with a mechanical huller (7) and the final samples of groats and hulls were carefully hand-picked.

Results

Sunflowerseed

Three samples of sunflowerseed were studied and the mean equilibrium moisture values for whole seed, meats, and hulls are shown graphically in Fig. 2. The actual values together with differences between meats and hulls are given in Table II. If moisture contents of the hulls and meats are plotted against moisture content of the whole seed, two virtually straight lines are

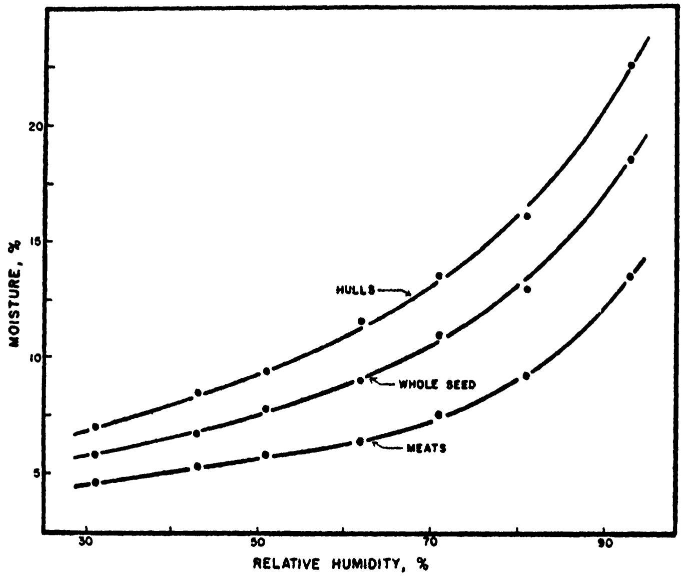

Fig 2 *Relation of the hygroscopic moisture in whole sunflowerseed, meats, and hulls to various relative humidities at 25° C.*

TABLE II

Relation of equilibrium moisture content of sunflowerseed, sunflower hulls, and sunflower meats to relative humidity at 25°C

Relative humidity, %	Moisture content, %			
	Whole seed	Hulls	Meats	Difference, hulls minus meats
31.0	5.8	7.0	4.7	2.3
43.0	6.7	8.4	5.3	3.1
51.0	7.8	9.3	5.8	3.5
62.0	9.0	11.6	6.4	5.2
71.2	11.0	13.6	7.6	6.0
81.1	12.9	16.2	9.2	7.0
93.0	18.5	22.6	13.5	8.1

obtained that diverge by the amount shown in the last column of Table II. This indicates that the distribution of moisture between meats and hulls is directly proportional to the total moisture of the seed.

A comparison of the curve for whole sunflowerseed with that obtained by Larmour, Sallans, and Craig (4) shows that the moisture values obtained in the present study are higher, especially at higher humidities. This may be due in part to the use of an aspiration instead of a static system for production of controlled humidities. However, it seems more probable that the main difference is caused by differences in the samples of seed used. For example, in the present study values of 5.4, 5.7, and 6.3% moisture were obtained at a relative humidity of 31%. Similar differences were observed at all the other humidity levels.

It appears that differences in kernel content of the seed and oil content of the meats must have an effect on the equilibrium moisture values. The data on hulls for the three samples showed much closer agreement than similar values for whole seed and meats, although one sample was consistently slightly higher than the other two. Since the hulls are composed mainly of cellulose and lignin and both of these materials appear to have similar moisture holding capacities, little variation in the equilibrium moisture values would be expected. For whole seed the oil content is approximately 25% and for meats, 50%. Since the oil has little, if any, tendency to absorb moisture, variations in the quantity present would alter the proportion of hygroscopic material with a resultant shift in equilibrium moisture values for whole seed and meats.

Oats

The data obtained for oats using a single sample are presented graphically in Fig. 3 and the differences between hulls and groats are shown in Table III. As with sunflowerseed a plot of hull and groat moistures against moisture content of the whole seed gives two straight lines. However, in this case the lines are virtually parallel as indicated by the constant difference between groats and hulls shown in the last column of Table III.

TABLE III

Relation of equilibrium moisture content of oats, oat hulls, and oat groats to relative humidity at 25° C

Relative humidity, %	Moisture content, %			
	Whole seed	Groats	Hulls	Difference, groats minus hulls
31.0	8.1	8.6	7.3	1.3
43.0	9.2	9.7	8.4	1.3
51.0	10.0	10.6	9.1	1.5
62.0	11.2	11.9	10.5	1.4
71.2	12.6	13.2	11.8	1.4
81.1	14.7	15.4	14.0	1.4
93.0	20.2	20.8	19.4	1.4

The other striking difference between oats and sunflowerseed is that with oats the meats have a higher moisture holding capacity at equilibrium than the hulls. This is just the reverse of the results obtained with sunflowerseed. Apparently these differences in behaviour are due mainly to differences in oil content of the various materials.

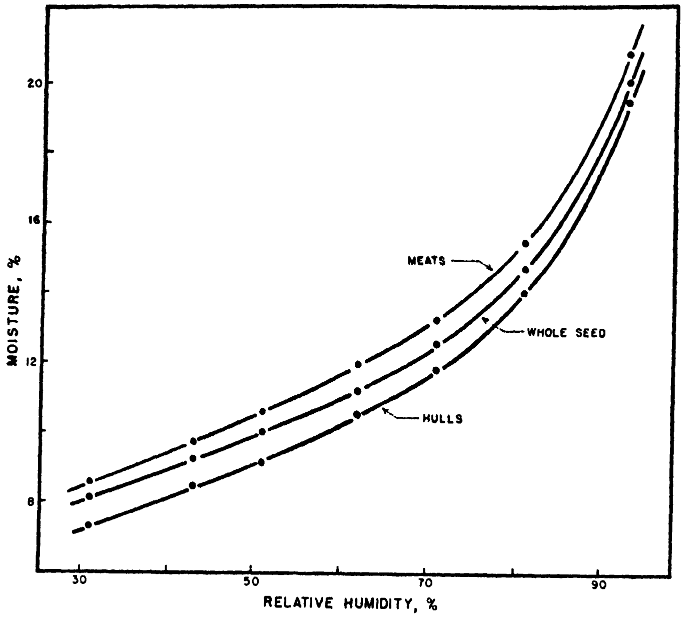

FIG. 3. *Relation of the hygroscopic moisture in oats, oat hulls, and oat groats to various relative humidities at 25° C.*

Relation of Hygroscopicity to Grain Constituents

In their studies on cereal grains Coleman and Fellows (2) were unable to relate differences in hygroscopic equilibria of grains to protein content. Subsequently Ramstad and Geddes (6) postulated differences in ash content as a possible cause of these differences. In their study Larmour, Sallans, and Craig (4) found that differences in ash content would not explain the differences in hygroscopicity of oil seeds when calculated to an oil-free basis and suggested that, "any adequate explanation of these differences will likely have to be found in the nature of the components of these seeds rather than in the actual amounts of the various components present".

In Table IV are collected data on sunflower hulls, oat hulls, wheat, oat groats, flax, and sunflower meats. Since oil does not absorb moisture, the values for oat groats, flax, and sunflower meats are expressed on an oil-free basis to facilitate comparison. Moisture values for wheat were estimated from the data of Coleman and Fellows (2), and values for flax were taken from the work of Larmour, Sallans, and Craig (4). The last two lines in the

TABLE IV

COMPARISON, ON AN OIL-FREE BASIS, OF THE HYGROSCOPICITY OF WHEAT, OAT GROATS, FLAX, SUNFLOWER MEATS, SUNFLOWER HULLS, AND OAT HULLS

Relative humidity, %	Moisture content, oil-free basis					
	Wheat	Oat groats	Flax	Sunflower meats	Sunflower hulls	Oat hulls
31.0	9.4	9.2	8.9	9.0	7.0	7.3
43.0	10.8	10.4	10.6	10.1	8.4	8.4
51.0	11.9	11.4	11.4	11.0	9.3	9.1
62.0	14.0	12.7	13.3	12.0	11.6	10.5
71.2	16.3	14.1	15.2	14.1	13.6	11.8
81.1	20.0	16.4	18.6	16.8	16.2	14.0
93.0	27.1	22.1	26.3	24.0	22.6	19.4
Protein, % (oil and moisture-free)	14.1	18.9	45.0	52.4	3.8	4.1
Ash, % (oil and moisture-free)	1.93	2.06	6.89	8.47	2.68	6.23

table show protein and ash content calculated to an oil- and moisture-free basis from average values for these materials (8).

The striking feature of the data is the close agreement in hygroscopic equilibria at low moisture values for all these materials, which differ so widely in composition. At humidities of 31.0, 43.0, and 51.0% the values for wheat, oat groats, flax, and sunflower meats are virtually the same even though the protein content differs by as much as 38%. Such variations as do occur bear no relation to total protein. A similar situation exists with respect to ash content. The only evidence that chemical composition may affect hygroscopicity is found in the case of oat and sunflower hulls. These materials show equivalent moisture holding capacities up to a relative humidity of 51%. However, their moisture values are approximately 2% lower than those for the other materials shown in Table IV. It would appear that radical changes in chemical composition, such as substitution of 50% protein for 50% cellulose, would be required to alter the hygroscopic moisture equilibrium at low relative humidities. Only the widest extremes in chemical composition of the material affect the moisture holding capacity.

This behaviour suggests that the water holding capacity is due to physical rather than chemical forces and that any adequate explanation for hygroscopic equilibria must consider grains as colloidal or gel systems. The observation that materials differing as widely in composition as wheat and sunflower kernels show similar hygroscopic equilibria up to a relative humidity of 51% or a moisture level of about 11.5% suggests that in this region the moisture may correspond to 'bound water'. Above this level the rate of moisture absorption with increasing humidity appears to be characteristic of the particular material under study. If it is assumed that 'capillary water' or 'water of imbibition' is present in this range, 'solvation' would occur and differences in the amounts of soluble electrolytes and organic constituents would begin to affect the water absorbing characteristics of the gel structure.

It is obvious that the hygroscopic behaviour of grains is a complicated phenomenon and no simple interpretation based on a single factor will provide an adequate explanation. However, it is interesting to note that Fairbrother (3) reports a linear relation between moisture content of wheat flour and relative humidities between 15 and 90%. Above 90% relative humidity a sharp rise in moisture uptake with increasing humidity was observed. In view of the results reported above it is difficult to conceive that this marked difference between the behaviour of wheat and flour can be explained on the basis of chemical constitution. However, since the cellular structure of wheat is destroyed in the milling process, it appears quite logical to attribute the difference in hygroscopic behaviour to changes in the physical state of the material. This may be taken as further evidence that the main factors influencing hygroscopicity of grains are colloidal and are related to the physical structure of the grain.

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FLASH DRYING IN RELATION TO HULLING OF SUNFLOWERSEED AND OATS[1]

By G. D. Sinclair[2] and H. R. Sallans[3]

Abstract

A laboratory flash drying unit with continuous feed is described In tests on sunflowerseed and oats it was possible to lower the moisture content of the hulls several units per cent without appreciably changing the moisture content of the meats. The effect of this change in the moisture distribution between meats and hulls on hulling efficiencies was studied. It was found that flash drying gave a slightly lower percentage of seed hulled with a definite decrease in the percentage of meats broken Furthermore, the damaged meats were not broken into as small pieces and hence separation of meats and hulls was facilitated.

Results of hygroscopic moisture studies on sunflowerseed and oats (1) have shown that a definite difference in moisture content exists between the kernels and the hulls. With sunflowerseed the moisture level in the hulls is higher than that in the meats, while with oats this distribution is reversed. It was suggested (3) that the ideal way to secure a high percentage of hulling with minimum breakage of meats was to have the hull dry and brittle with the meats moist and tough

Preliminary experiments on drying small samples of sunflowerseed in an air oven with forced circulation showed that the normal moisture distribution between meats and hulls could be changed by short periods of drying at moderate temperatures. It was possible under favourable conditions to reduce the moisture content of hulls several per cent without changing the meat moisture appreciably. In view of these findings, it was decided to construct a small unit to study the effects of flash drying in relation to hulling. Since oats are often pan dried before hulling and the normal moisture distribution is the opposite to that in sunflowerseed, it appeared that data on oats would be of value in assessing the utility of flash drying.

To produce the maximum drying of the hull with a minimum change in the moisture content of the meats, it is necessary to subject the seed to a short, sharp heating period and to dehull it promptly before moisture diffuses from the kernel back into the hull In preliminary trials the seed was dropped directly from the heating unit into the huller This was unsatisfactory as the hulls seemed to sweat on cooling slowly. A greater moisture differential between meats and hulls was obtained by cooling the seed in a blast of air immediately after heating

The design of the unit and data on changes in moisture distribution and hulling efficiencies are presented in the following sections of this paper

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Equipment

A section drawing of the flash drying unit is shown in Fig. 1. A three-bladed 6 in. centrifugal fan, *F*, is connected to a duct containing two flues. The upper one opens into the drying chamber, *B*, and is heated by four 660-w. cone type heaters while the lower one opens into cooling chamber *C*. A feed hopper, *A*, is mounted above drying chamber *B* and a release roll is mounted below cooling section *C*.

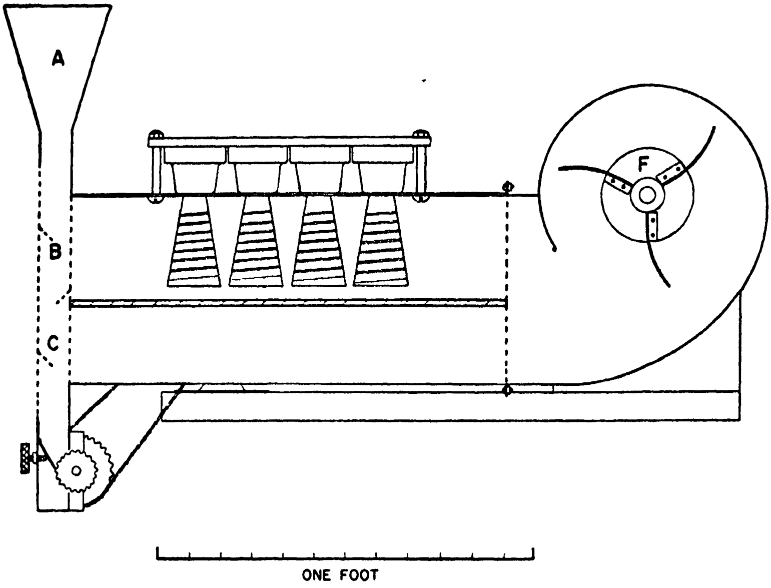

Fig. 1. *Section drawing of flash drying unit.*

The blades of fan *F*, made of 16-gauge sheet metal, are mounted on a steel flange carried on the shaft of a ¼ h.p., d-c. motor. Regulation of air flow is obtained by adjustable slides on the air inlet to the fan housing. This housing, having an air outlet 3 in. by 6 in., is fabricated from 20-gauge sheet metal and is bolted to the heating and cooling ducts. A sheet of galvanized screen with 1/16 in. perforations is inserted between the fan and air ducts to provide a back pressure and thus give a uniform distribution of air. The heating and cooling ducts, made of 20-gauge galvanized iron, are separated by a 3/16 in. transite board and the whole unit is covered with 10 layers of heavy asbestos paper. The drying and cooling unit is faced with galvanized screen having 1/16 in. openings and carries three horizontal fins to mix the seed as it passes through the dryer. The inner screen area, 3 in. × 6 in., is smaller than the outer area, 3 in. × 8 in., to provide a pressure drop across the unit. This facilitates a uniform rate of feed and prevents clogging. A grooved wooden release roll is chain driven from a 1/30 h.p. variable speed motor that can be reduced to 30 r.p.m. Feed rate is controlled by adjusting the clearance between the roll and a hinged metal flap by means of a thumbscrew.

After a few preliminary trials the equipment was adjusted to give an air temperature of 190° to 195° C. when no seed was passing through chamber *B*. Air velocity under these conditions was 400 to 410 linear feet per minute in both the heating and cooling sections. When the unit was filled with sunflowerseed the air velocity was 250 ft./min. and with oats 240 ft./min. as measured with an anemometer. Actual operating temperatures recorded by a thermometer inserted in the centre of heating section *B* varied from 121° C. to 175° C. depending on the moisture content of the seed and the rate of feed.

Materials and Methods

Sunflowerseed

A two bushel lot of No. 1 C.W. Mennonite sunflowerseed, 52.5% meats (dry basis), was obtained from a local processing firm. After careful cleaning to remove trash, the sample had a bushel weight of 26.4 lb. and was of fairly uniform seed size. The bulk sample was thoroughly blended in a rotary mixer and quartered. The main samples were tempered to moisture levels of 8.0, 9.4, 10.6, and 12.2%. After tempering, each of these samples was divided into four equal parts to provide material for four drying rates.

Oats

Two bushels of commercial Banner oats of seed grade, 68.8% groats (dry basis), was obtained from the Field Husbandry Department at the University of Saskatchewan. The sample as received was cleaned to seed specifications and had a bushel weight of 41.9 lb. After thorough mixing it was subdivided as for sunflowerseed, but the moisture levels selected were 9.8, 12.0, 14.1, and 16.3% since oats normally have a higher percentage of moisture than sunflowerseed (1).

Drying

The drying portion of the unit, consisting of both the heating and cooling sections, was found to hold 175 gm. of sunflowerseed or 278 gm. of oats. The release was set so that these quantities of material passed through the drying unit in 0.5, 1.0, 1.5, and 2.0 min., respectively, for the tests on both sunflowerseed and oats at each moisture level. It follows that the drying times recorded represent the time for the seed to pass through both heating and cooling sections of the dryer. Furthermore, the actual exposure of the seed to air at 190° to 195° C. is just a little greater than half the total drying time. For example, a drying time recorded as 0.5 min. represents 17 to 18 sec. heating followed by 12 to 13 sec. cooling. Under these conditions it was observed that the meats were only slightly warmed. On exposure for 70 sec. in the longest drying time of 2.0 min. there was no indication of damage to the meats in either sunflowerseed or oats even at the lowest moisture level of the feed.

Before starting a test the dryer was allowed to run till it was thoroughly heated, and seed was then fed continuously until a thermometer inserted in chamber *B* showed a constant reading. At this point samples were taken for determinations of moisture content and hulling efficiency. Samples were hulled immediately after drying, only sufficient time being taken to weigh a 100 gm. aliquot.

Hulling

Tests on hulling efficiency were made with a laboratory huller and the methods of estimating percentage of seed hulled and meats broken have been described (3). A huller speed of 3000 r.p.m. was used for sunflowerseed and 3400 r.p.m. for oats.

Determination of Moisture

Determination of moisture content on the whole seed presented no difficulty. In the hulling and fanning operations, however, it is obvious that, if the relative humidity of the laboratory air differs markedly from that in equilibrium with the moisture content of the seed (1, 2), the values obtained for meats and hulls will not represent the moisture distribution in the seed at the time of impact in the huller. Moisture content of the hulls was found to change markedly on fanning, but tests on sunflower meats indicated that fanning produced only small changes, 0.2 to 0.3%, in moisture level. Hence, values for moisture content in the hulls were computed from data on meat moisture, whole seed moisture, and kernel percentage of the seed.

Results

Drying

Data on sunflowerseed at four moisture levels and four drying treatments are shown in Table I. If the moisture contents of the tempered undried sunflower samples are compared with equilibrium moistures from hygroscopic studies (1) it is found that 8 0, 9 4, 10.6, and 12.2% moisture in the whole seed correspond with relative humidities of 53, 64, 71, and 78%. It will also be noted that the moisture values for meats are consistently lower than those given in the previous data, while the hulls are consistently higher. This would be expected since the sample used in the present investigation had a higher percentage of kernels than the samples previously used, 52 5% as compared with about 47%.

Since little, if any, loss in moisture content of the sunflower meats occurred during hulling and fanning, it is apparent that the moisture distribution between meats and hulls of the tempered samples corresponded to equilibrium conditions.

Results for oats appear in Table II. From comparison with hygroscopic data (1) it appears that normal oat moistures of 9 8, 12 0, 14 1, and 16.3% should be in equilibrium with relative humidities of 48, 67, 78, and 86%. An examination of the data for hulls and groats shows that at a moisture level of 9.8% the values agree with those expected from previous work. However, as the moisture content is increased, there is an apparent reversal in moisture distribution, i.e., at 14.1% and 16 3% the hulls are higher in moisture than the groats. This is due to relatively rapid drying of the oat groats in hulling

TABLE I

THE EFFECT OF FLASH DRYING ON THE MOISTURE DISTRIBUTION BETWEEN SUNFLOWER MEATS AND HULLS AND ON HULLING EFFICIENCIES

Moisture in original seed, %	Drying time, min.	Moisture in dried seed, %			Hulling, %	Broken meats, %
		Whole seed	Meats	Hulls		
8.0	0.0	8.0	5.7	10.4	91.4	16.8
	0.5	7.1	5.6	8.6	91.8	17.2
	1.0	6.1	5.5	6.7	94.4	23.3
	1.5	5.0	5.1	5.0	94.4	25.5
	2.0	4.6	4.8	4.4	97.3	32.1
9.4	0.0	9.4	6.3	12.7	87.9	10.2
	0.5	8.1	6.4	9.9	86.8	12.0
	1.0	7.3	6.3	8.5	91.0	16.5
	1.5	6.1	6.0	6.3	94.4	22.2
	2.0	5.5	5.8	5.2	96.4	23.8
10.6	0.0	10.6	7.3	13.9	79.2	4.3
	0.5	9.7	7.3	12.2	83.7	6.8
	1.0	8.5	6.9	10.2	89.1	11.9
	1.5	7.4	6.8	8.1	89.5	13.3
	2.0	6.0	6.4	5.6	93.7	17.6
12.2	0.0	12.2	8.0	16.4	69.0	2.3
	0.5	10.6	8.0	13.2	68.2	3.9
	1.0	9.4	7.7	11.2	80.0	6.1
	1.5	7.8	7.4	8.3	86.8	9.4
	2.0	6.6	7.0	6.3	90.8	13.0

TABLE II

THE EFFECT OF FLASH DRYING ON THE MOISTURE DISTRIBUTION BETWEEN OAT GROATS AND HULLS AND ON HULLING EFFICIENCIES

Moisture in original seed, %	Drying time, min.	Moisture in dried seed, %			Hulling, %	Broken meats, %
		Whole oats	Groats	Oat hulls		
9.8	0.0	9.8	10.5	8.2	94.9	20.3
	0.5	9.3	10.4	6.6	93.6	12.6
	1.0	9.0	10.2	6.3	95.0	15.9
	1.5	7.8	9.5	4.0	96.2	22.0
	2.0	7.6	9.2	3.7	98.8	32.8
12.0	0.0	12.0	12.1	11.6	87.3	8.8
	0.5	11.3	12.1	9.3	86.4	6.8
	1.0	10.5	11.6	8.0	90.8	8.0
	1.5	9.4	11.0	5.7	94.6	15.8
	2.0	8.4	10.3	4.0	96.6	22.7
14.1	0.0	14.1	13.8	14.8	75.0	3.6
	0.5	13.4	13.7	12.8	77.4	4.1
	1.0	12.3	13.1	10.3	87.0	6.1
	1.5	11.4	12.4	9.3	92.2	12.0
	2.0	9.9	11.2	6.9	96.8	22.5
16.3	0.0	16.3	15.4	18.3	63.9	2.6
	0.5	15.2	15.2	15.2	71.0	1.9
	1.0	14.1	14.8	12.4	82.2	2.9
	1.5	12.3	13.7	9.0	92.6	8.9
	2.0	10.9	12.8	6.0	93.8	16.1

and fanning, which results from a higher surface to volume ratio and a lower oil content than is found in sunflower meats.

The data on moisture distribution in Tables I and II show clearly that it is possible by means of flash drying to reduce the moisture levels in both oats and sunflowerseed to a marked degree without appreciably affecting the moisture level in the meats. The degree of drying is obviously a function of the original moisture level in the seed and the drying time.

To facilitate comparison of the data on moisture distribution, mean values at each drying rate over all four initial moisture levels are shown graphically in Fig. 2 for both sunflowerseed and oats. The most striking and interesting feature is the close similarity in drying rate between sunflower and oat hulls. In both cases the initial moisture content of approximately 13.0% dropped rapidly in an almost linear relation with drying time. The curves for sunflower and oat hulls in Fig. 2 are almost parallel and in both cases the moisture drop was exactly 8.0%.

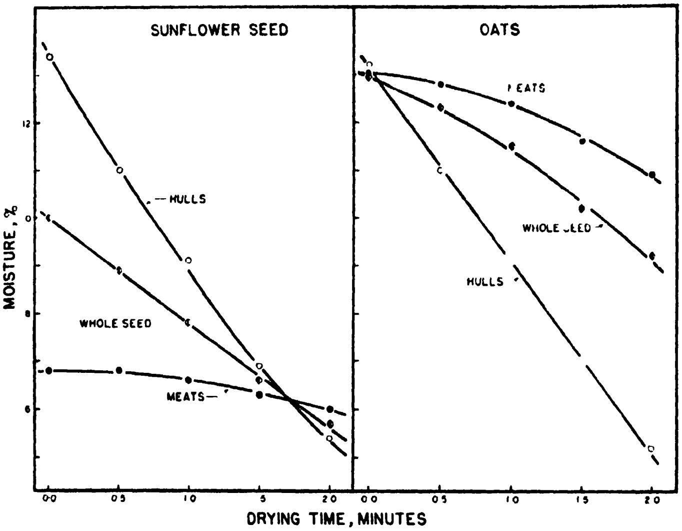

FIG. 2. *Distribution of moisture between hulls and meats of sunflowerseed and oats for various levels of flash drying.*

The moisture drop for oat groats is 2.1% while that for sunflower meats is only 0.8%. Since oat groats at 13% moisture are in equilibrium with a relative humidity of approximately 73% while for sunflower meats at 6.8% the corresponding value is 68%, the observed difference in drying rate cannot be due to differences in the moisture holding capacity of the two materials. It would seem that there is a greater transfer of moisture from the groats through oat hulls than from meats through sunflower hulls.

With sunflowerseed a drying time of two minutes produced a change in the differential moisture level between hulls and meats of + 6.4 to −0.6, or a total change of 7.0%; the corresponding value for oats was from −0.2 to −5.7, or a total of 5.5%.

Hulling

Data showing the percentage of seed hulled and meats broken at each drying level are shown in Table I for sunflowerseed and in Table II for oats. It will be noted that for sunflowerseed there is a consistent increase in the percentage of seeds hulled with increased drying time, but this is accompanied by an increase in the percentage of meats broken. With oats a similar trend is evident; however, at the lower moisture ranges, 9.8 and 12.0%, there appears to be a drop in broken meats for the shorter drying times.

To facilitate comparison of hulling efficiencies for flash-dried seed with those for seed having a normal moisture distribution, mean values over the four initial moisture ranges are plotted against percentage moisture in Fig. 3.

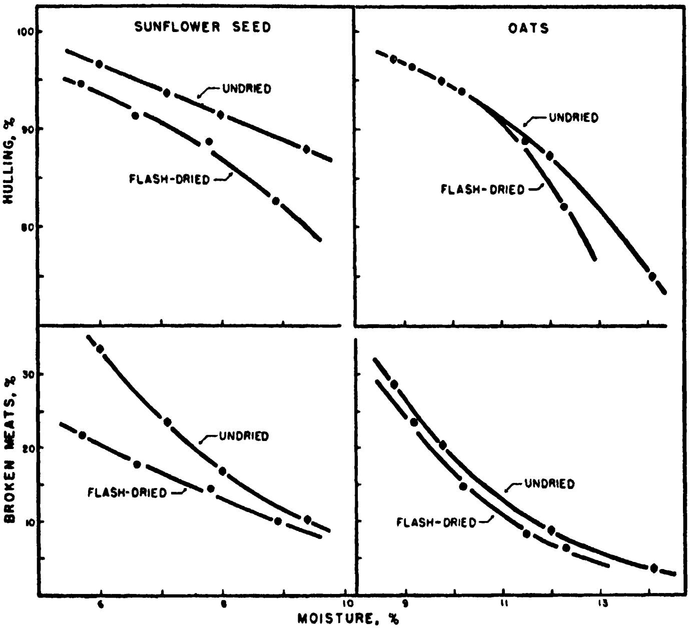

FIG. 3. *Relations of percentage seed hulled and meats broken to moisture content of normal and flash dried sunflowerseed and oats.*

The curve representing the percentage hulling for flash-dried seed falls below that for seed having normal moisture distribution. At 5.5% total moisture the flash-dried seed shows 2% less hulling while at 9.0% the difference is 10.0%. Data for percentage of broken meats in the lower figure show that at 5.5% moisture there is a reduction of 11% in breakage due to flash drying, but at 9.0% this difference falls to 2.0%. The same general trend is shown for the data on oats, but the differences between dried and undried samples are considerably smaller than those for sunflowerseed.

It should be noted that the broken meats from flash-dried samples were not broken into as small pieces as those from samples having a normal moisture distribution. Hence, in any recovery system involving fanning there would be an appreciably greater recovery of oil-bearing material from flash-dried seed than the analytical figures quoted would indicate.

Discussion

It has been shown that the normal differential in moisture content between hulls and meats can be radically changed by means of flash drying. The primary objective of securing drier hulls with moister meats was attained. However, data on hulling efficiencies show that the expected result of higher percentage hulling at comparable moisture levels was not realized.

Normally in Mennonite sunflowerseed the meat is held firmly to the hull at one or more points of contact, while there is free space between the meat and hull over the remaining area. If there is free space under the point of impact in the huller, the hull crumples and cracks under the impact with little damage to the meat. When seed is flash dried, the hull tends to shrink with no compensating decrease in volume of the meat. Under these conditions the hull area not directly in contact with the meat is reduced and even though the hull is drier and more brittle the additional support furnished by the meat tends to resist the shattering effects of impact. In addition sunflower hulls have a light, spongy interior lining that is particularly susceptible to changes in moisture content. When seed is flash dried the atmosphere between the hull and meat becomes saturated with moisture at elevated temperatures. When it is cooled this moisture condenses in the spongy lining of the hull, which becomes tough. Even though the outer hull may become more brittle the shattering effect of impact is lessened by the tough inner lining with the result that the seed cracks but the hull is not completely freed from the meat.

In oats there is less free space between the meats and hulls than in sunflowerseed and oat hulls do not have the same spongy lining as sunflower hulls. Hence, the effects noted for sunflowerseed are not as pronounced for oats. At the more intensive drying levels it was noted that the hulls tended to shrink so tightly onto the meats that they cracked or loosened. This probably accounts for the fact that at these drying levels the curves for percentage hulling of dried and undried seed coincide.

The definite and consistent lowering in the percentage of broken kernels is a reflection of an increased toughness or plastic quality in the meats. This effect is more noticeable for sunflowerseed since less drying of the meats occurred than in oats, and the high oil content of sunflower meats also imparts plasticity. On sharp impact this property causes the meats to break into two or three relatively large fragments as contrasted with the shattering effect that occurs at lower moisture levels.

It appears that with suitable adjustment of temperatures and drying times the moisture in the hulls of both sunflowerseed and oats can be materially reduced without changing the meat moisture appreciably. On hulling this gives no material gain in percentage of seed hulled but can give a significant lessening of shattering damage to the meats. Thus the main advantage of flash drying is to simplify separation of meats and hulls.

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PACKAGING

VII. WATERPROOFING OF FIBREBOARD CONTAINERS[1]

BY C. G. LAVERS[2]

Abstract

An attempt was made to find a material in which domestic fibreboard cartons could be dipped to produce waterproof packages. The waterproofing agents tested included vinyl resins, cellulose acetates, nitrocelluloses, polystyrene, chlorinated rubber, corn protein – resin, a wood oil drier combination, an alkyd, and microcrystalline wax. Agents that did not coat the surface of the box, or gave only a very light coating, were not satisfactory. Wax could not stand rough handling at low temperatures. Two nitrocellulose formulations and one vinyl resin solution were found to be particularly suitable for this application. One of the nitrocellulose waterproofing agents dried at room conditions in 15 min., and boxes coated with it withstood water immersion for over 30 days after rough handling at −40° F. This method of producing waterproof packages appears to be quite practical.

Introduction

During the war, because of uncertain conditions of handling and warehousing, many tons of warlike stores had to be shipped in waterproof containers. One of the most common methods employed in making waterproof packages was by wrapping the product to be protected, either before or after placing it in a carton, in Grade *C* material (Cellophane laminated to scrim cloth and coated on both sides with microcrystalline wax), sealing by dipping in wax, and overwrapping with kraft paper to prevent packages from sticking together. This method was expensive, and labour and time consuming. Hence, it was felt desirable to attempt to find a material in which domestic fibreboard cartons could be dipped to produce a waterproof package that would require no further processing. Several commercial waxy and resinous products were tested for this application, and this paper presents the results.

With the cessation of hostilities and consequent improvement in shipping conditions, the need for waterproof packages was greatly reduced and hence this project was not continued. For this reason, the results presented are not as complete as they might otherwise have been; however, they do serve to indicate the performance that may be expected from various types of waterproofing agents and also show the practicability of this method of packaging.

Materials and Methods

It was believed that a material for the purpose described above should have as many of the following properties as possible. It should preferably be applied without heating; should dry rapidly; should require no overwrap

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[2] *Chemical Engineer, Food Investigations.*

to prevent packages from sticking together (blocking); should retain flexibility at low temperatures; and it should not soften and run off the package at high temperatures (140° F.).

The materials tested were of three general types: solvent deposited resins that left a surface film over the entire package, impregnating materials that left little or no surface coat, and wax. The agents tested included: vinyl resins, cellulose acetate, nitrocelluloses, polystyrene, chlorinated rubber, corn protein – resin, a wood oil drier combination, an alkyd, and microcrystalline wax. Further details are given in Table I.

An initial test of all samples was done as follows. Regular flat folding cartons with full overlapping long flaps (0.02 in. chip board; dimensions, 4 × $2\frac{3}{4}$ × 1 15/16 in.; opening end, $2\frac{3}{4}$ × 1 15/16 in.) were filled with sawdust and closed with silicate glue. Seams around the top and bottom, and at the side, were sealed with a waterproof pressure sensitive tape, and the box was then dipped in the waterproofing agent under test, one-half at a time, allowing at least a $\frac{1}{2}$ in. overlap. Each material was tested both as a single and as a double coating. The waterproofing agents were allowed to dry at room temperature without forced draft for approximately the time indicated in Table I. The boxes were then immersed in water and left until failure, or for one month, whichever period was shorter.

Those materials that showed promise in the initial test were subjected to a rough handling test. Four cartons were given a single dip, and four a double dip in the medium. The packages were then placed in a wooden master container capable of holding 32 packages (two layers, each accommodating four by four cartons). The master container was a style two nailed wood box, constructed according to Canadian Packaging Committee Code No. 11.* The test packages were placed along the side of the box, and excess space in the centre was filled with dummy cartons containing sawdust. The loaded master container was stored at −40° F. overnight, followed by subjection to 20 free falls of three feet each (five falls on each long edge). Test packages were then removed from the wooden box, allowed to reach room temperature, and immersed in water.

As a further test of flexibility, the agents used in the rough handling test were subjected to a low temperature bend test. For this trial, strips of 50 lb. kraft (ream weights refer to 500 sheets, 24 × 36 in.) 1 in. by 8 in. were given single and double dips in the waterproofing medium, allowed to dry, stored at the temperature of test (−10° F. and −40° F.) for two hours, bent quickly (less than one second) around a $\frac{1}{2}$ in. diameter rod, and then examined for cracking or flaking.

An accelerated ageing test was also done on these materials. Single and double dipped packages were stored at 140° F. (low humidity, approximately 6%) for one month, and then subjected to water immersion.

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* *Boxes, Wooden, Nailed. Can. Packaging Committee Code 11. Currently available from Forest Products Laboratories, Dept. of Mines and Resources, Ottawa, Canada.*

TABLE I

INITIAL TEST OF WATERPROOFING AGENTS

(Each result based on two packages)

Material	Approximate drying time, hr.	Results of water immersion, time (days) to failure with:	
		Single coat	Double coat
A. Vinylite resin in xylol, methyl ketone, and methyl isobutyl ketone	0.5	<1	<1
B. Vinyl resins in organic solvents containing added pigments and plasticizers	1.5	6	>30
C. Vinyl chloride acetate copolymer, high molecular weight, dissolved in acetone, plasticized	1.0	9	18
D. Vinyl resin emulsion plus solvents, plasticized	1.0	<1	<1
E. Vinyl resin emulsion plus solvents, plasticized	1 0	<1	<1
F. Vinyl and vinylidene resins in acetone and acetate solvents	1.5	>30	>30
G. Cellulose acetate dope	2.5	2	7
H. Cellulose acetate in acetone and other solvents, plasticized	18	2	16
Ia. Nitrocellulose, 21-22% non-volatile, in a solution of esters, alcohols, and hydrocarbons, plasticized	2 0	>30	>30
Ib. Nitrocellulose, 13% non-volatile, in a solution of esters, alcohols, and hydrocarbons, plasticized	2 0	>30	>30
J. Nitrocellulose in a mixture of ester solvents, plasticized	0 25	18	15
K. Styrene resin solution	2 0	<1	<1
L. Chlorinated rubber solution, plasticized	0.25	<1	<1
M. Corn protein – resin solution	1.0	<1	<1
N. Treated wood oil drier combination (leaves no surface film)	1 5	<1	<1
O. Alkyd, phthalic anhydride content 34% (on solid basis), linseed oil modified, petroleum spirit solvent	48	<1	<1
P. Microcrystalline wax: softening point, 150°-155° F.; penetration (100 gm. at 77° F.), 40-45; flexibility good, see Table III	1-2 Min.	<1	6

Since the shortest drying time possible would be desirable in the application of these materials, the drying time of the more promising samples was determined by a blocking test. Strips of 50 lb. kraft, 1 in. by 4 in., were dipped in the waterproofing material and allowed to dry under room conditions for a measured time. At the end of this time, four of these strips were placed on top of each other, and a 1 lb. weight was placed on top of the pile. The samples were stored at 120° F. overnight, then cooled to room temperature, and examined for blocking (sticking together). If blocking did not occur the drying time was reduced until samples just stuck together after this treatment.

Results

Waterproofing materials that left no surface coating on the box, such as *N* (Table I), failed to produce a watertight package because they did not seal the seams and corners of the boxes. Similarly agents that did leave a surface film but had very low viscosity failed to seal the seams because most of the waterproofing compound ran off the box before it had a chance to dry. Materials in this category were *A*, *L*, *O*, and probably *K*. The vinyl resin emulsions (*D*, *E*) were not satisfactory.

On the basis of the initial test for water resistance (Table I), nine of the materials appeared more promising than the rest and were selected for further study. These nine materials are listed in Tables II and III. The rough handling and ageing tests (Table II), indicated that waxes would not be suitable for this purpose if severe handling conditions were encountered. Agents *B*, *F*, *G*, and *H* were also severely affected by these tests. In addition materials *B*, *F*, and *H* all required over 15 hr. to dry (Table III), which further detracted from their value. It is possible that drying times might have been

TABLE II

ROUGH HANDLING AND AGEING TEST OF PACKAGES TREATED WITH WATERPROOFING AGENTS

(Each result based on four packages)

Material	Results of water immersion after rough handling Time (days) to failure with:		Results of water immersion after ageing Time (days) to failure with:	
	Single coat	Double coat	Single coat	Double coat
B	<1	<1	20	>30
C	20	>30	>30	>30
F	2	4	>30	>30
G	<1	10	6	10
H	<1	<1	8	8
Ia	<1	>30	>30	>30
Ib	<1	>30	>30	>30
J	>30	>30	>30	>30
P	<1	<1	<1	<1

TABLE III

FLEXIBILITY AND MINIMUM DRYING TIME OF WATERPROOFING AGENTS

Material	Temperature of bend test				Minimum drying time, hr.
	−10° F.		−40° F.		
	Single coat	Double coat	Single coat	Double coat	
B	Pass	Pass	Pass	Cracked	>15
C	Pass	Pass	Pass	Pass	1.0
F	Pass	Pass	Pass	Pass	>15
G	Pass	Pass	Pass	Pass	0.75
H	Pass	Pass	Pass	Cracked	>15
Ia	Pass	Pass	Pass	Pass	0.75
Ib	Pass	Pass	Pass	Pass	0.75
J	Pass	Pass	Pass	Pass	0.25
P	Pass	Pass	Pass	Cracked and flaked	—

reduced somewhat by using forced air circulation and heating devices, but under these conditions it was difficult to avoid the formation of bubbles in the coating when the solvent evaporated rapidly. The approximate drying time given in Table I does not always agree with that in Table III because the time shown in Table I is the time required for the material to be dry to the touch, whereas Table III gives the drying time required to eliminate blocking. Materials *J*, *C*, *Ia*, and *Ib* (the last two as double coats) appeared to be superior to the other agents and their relative merit fell in that order. It will be noted that all of these except *C* were nitrocellulose formulations, and *C* was a vinyl resin solution. However, it seems likely that some of the other materials tested such as chlorinated rubber, cellulose acetate, and polystyrene could have been improved considerably by changing their composition somewhat, i.e., by better plasticizing, or by increasing the viscosity either by increasing the non-volatile content of the solution or by using more highly polymerized resin.

The results indicate that this method of making waterproof packages would probably work quite satisfactorily using a waterproofing compound such as *J*, which required only 15 min. to dry under room conditions, and produced packages that withstood water immersion for over 30 days after rough handling at −40° F.

Acknowledgments

The author wishes to express his gratitude to Dr. J. A. Pearce of these laboratories for his kind advice, and to Mr. R. F. Plante for his technical assistance.

ANTIMONY TRICHLORIDE-ETHANOL PRECIPITATION FOR THE FLUOROMETRIC DETERMINATION OF RIBOFLAVIN IN PORK[1]

By Jessie R. Lewis[2] and Paul R. Gorham[3]

Abstract

A fluorometric method suitable for routine analyses is presented in which interfering substances in papain–takadiastase extracts of pork are precipitated in the presence of 0 02% antimony trichloride and 47 5% ethanol. Antimony trichloride prevents the adsorption of riboflavin upon the precipitate Recoveries of 95 to 100% are obtained Determinations by this method correlate well with those obtained microbiologically for eight samples of fresh pork, four cooked, and four uncooked, $r =$ 94, for 20 samples of cured pork, four cooked, and 16 uncooked, $r =$ 98

Introduction

The fluorometric determination of riboflavin in materials of low potency such as pork is made difficult by the relatively high proportion of pigments and other fluorescing substances that accompany riboflavin on extraction. Various techniques have been used, both singly and in combination, for minimizing the effect of these interfering substances: solvent extraction (6, 9, 13, 15, 26), adsorption and elution (1, 2, 3, 4, 10, 11, 12, 16, 21), precipitation (11, 13, 15, 23), permanganate oxidation (1, 2, 3, 5, 10, 11, 12, 16, 17, 18, 21, 24), and stannous chloride reduction (9, 15, 24). Usually, a correction must be applied for the fluorescence of non-riboflavin materials that still remain Methods for destroying or quenching the fluorescence of riboflavin to obtain this correction factor include photolysis (7, 8, 21), reduction with sodium hyposulphite* (15, 17, 26), and treatment with strong alkali (19).

A proposed study of the effect of various curing methods on the retention of several of the B-complex vitamins in pork muscle required a rapid riboflavin assay that would give results in good agreement with those obtained by slower microbiological methods The time-consuming adsorption and elution step frequently used for low-potency materials was avoided since complete adsorption of riboflavin from the extract is questionable (3, 16). Extensive trials of several existing methods (15, 19, 22, 23) gave unsatisfactory results. This led to the development of the following procedure, which utilizes a portion of the papain–takadiastase extract used for assaying other members of the B-complex

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* *$Na_2S_2O_4$ $2H_2O$, often sold as sodium hydrosulphite, powdered.*

Procedure

Weigh into a 250 ml. centrifuge tube 5 to 15 gm. of minced sample and add 100 ml. of acetate buffer, pH 4 6, containing 0.4% of a mixture of equal parts of papain and takadiastase. Digest at 37° C. with constant agitation for 16 hr. Filter through Whatman No. 12 paper into a 200 ml. volumetric flask, adjust pH to 6 8 with 4 to 5 ml. *N* sodium hydroxide, and make up to volume.

Transfer a 25 ml. aliquot of this extract to a 100 ml. centrifuge tube. From automatic burettes add, with constant swirling, 1 ml. of 1% antimony trichloride in absolute ethanol followed by 24 ml. of 95% ethanol. Stopper the tubes, allow 15 min. for precipitation (preferably in the cold), and then centrifuge for five minutes at 2000 r.p.m.

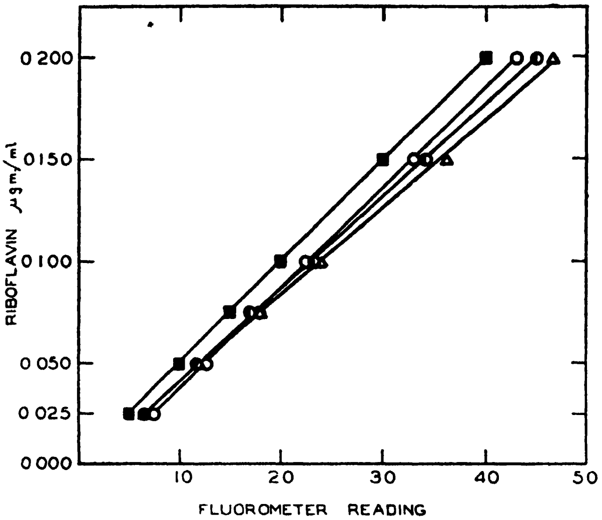

FIG 1 *Riboflavin reference curves for various solvents Water or 0 02% antimony trichloride in 47 5% ethanol* ■, *47 5% ethanol* ○, *23 75% ethanol* ◐, *50% acetone* △. *Each value is the mean of duplicate determinations*

Take a 10 ml. aliquot of the supernatant liquid and determine its fluorescence with a Coleman No. 12 photofluorometer, using 0 1 μgm. per ml. sodium fluorescein to set the instrument at a reading of 50. Have all samples at room temperature when determining fluorescence. For the blank correction, add 0.25 ml. of a freshly prepared ice-cold solution containing 2 gm. sodium hyposulphite and 0 7 gm. of sodium bicarbonate in 20 ml. of water. Mix thoroughly, determine the residual fluorescence, and subtract this reading from that initially obtained. From an antimony trichloride – ethanol dilution curve (Fig. 1) convert this difference into concentration in micrograms per millilitre and multiply by the dilution factor to obtain the riboflavin content of the sample.

The importance of obtaining the blank correction with as little change in hydrogen ion concentration as possible needs to be emphasized. The use of strong alkali (19) to shift pH to 11 may largely destroy the fluorescence of riboflavin, but may equally well affect the fluorescence of the non-riboflavin materials being assessed. Moreover, with pork extract, it was found to create a turbidity that affected the precision of measurement. The use of 10 to 20 mgm. of solid sodium hyposulphite (4, 17) has been recommended, but addition by means of a solution is more convenient. Sodium hyposulphite readily decomposes in water, producing an acid solution that diminishes the fluorescence of non-riboflavin materials in pork extract. The recommended solution of sodium hyposulphite is stabilized somewhat by the sodium bicarbonate. It has a pH of 6.55, and the addition of 0.25 ml. to 10 ml. of extract at pH 6.8 does not alter the hydrogen ion concentration appreciably.

It should be noted that riboflavin in antimony trichloride – ethanol solution appears to the eye to have its yellow-green fluorescence masked by the blue fluorescence of the solvent. However, the sharp cutout of the filter transmitting fluorescent light, 90% transmission at 5400 Å to 0% at 5100 Å, excludes all measurement of the blue fluorescence (18).

Experimental

Initial attempts were made to clear extracts of cured pork by treatment with acetone or ethanol. Thirty-gram samples from eight different cures were extracted with papain–takadiastase, filtered, and each made to a volume of 200 ml. Aliquots of 25 ml. from six of the extracts were precipitated by an equal volume of acetone, and from four of the extracts by an equal volume of 95% ethanol. The solutions were filtered through Whatman No. 12 paper and the fluorescence of the filtrates was measured. Since riboflavin fluoresces more strongly in acetone or ethanol solution than it does in water (Fig. 1), the measurements were referred to dilution curves for the appropriate solvent in order to calculate the riboflavin content of the samples. Comparative microbiological determinations* were made upon the eight extracts. The results, expressed on a fresh-weight basis, are presented in Table I. The solvent precipitation and microbiological values were generally in poor agreement.

Significant losses of riboflavin occurred when small amounts of phosphotungstic acid, silver nitrate, copper hydroxide, or zinc hydroxide were added to pork extract treated with ethanol. The addition of 10 to 30 mgm. of antimony trichloride to 50 ml. of a mixture of equal parts of pork extract and 95% ethanol, however, appeared to improve clarification without causing loss of riboflavin.

Six uncooked (15 gm.) and three cooked (10 gm.) samples of cured pork were extracted and each made to a volume of 200 ml. Two aliquots of 20 ml. were taken from each extract. Five millilitres of water containing 5 μgm.

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* *All microbiological determinations were made by the method of Snell and Strong (25) modified by additions to the basal medium.*

TABLE I

COMPARATIVE RIBOFLAVIN ASSAYS OF CURED PORK BY THREE DIFFERENT METHODS, CALCULATED ON A FRESH-WEIGHT BASIS

Sample	Acetone precipitation			Ethanol precipitation			Micro-biological
	Reading	Blank	μgm./gm.	Reading	Blank	μgm./gm.	μgm./gm.
1	28.5	8.0	1.1	—	—	—	1.6
2	37.0	9.5	1.5	—	—	—	1.9
3	53.5	7.5	2.6	—	—	—	4.0
4	45.0	7.5	2.1	—	—	—	3.2
5	25.5	6.5	1.1	25.5	4.5	1.2	2.0
6	30.0	7.5	1.3	32.0	6.5	1.5	2.5
7	—	—	—	55.0	10.0	2.8	3.7
8 (*a*)	—	—	—	20.5	1.5	2.2	3.6
8 (*b*)	—	—	—	19.5	1.5	2.1	3.6

of riboflavin was added to one aliquot and 5 ml. of water was added to the other. All samples were cleared by the addition of 1 ml. of 1% antimony trichloride in absolute ethanol followed by 24 ml. of 95% ethanol, and centrifuging at 2000 r.p.m. for five minutes. An aliquot of the supernatant solution was taken and its fluorescence determined. The amount of riboflavin in 20 ml. of extract was calculated from a reference curve for 0.02% antimony trichloride in 47.5% ethanol (Fig. 1). The fluorometer readings, blank corrections, amounts of riboflavin per aliquot, and percentage recovery are given in Table II. By repeatedly checking the photofluorometer against the fluorescein standard, and making all readings to the nearest 0.25 of a scale division, recoveries of 95 to 100% were obtained.

A somewhat different form of recovery experiment was performed upon an extract of fresh pork to compare the effects of clarification by ethanol, acid

TABLE II

RECOVERY OF RIBOFLAVIN ADDED TO EXTRACTS OF CURED PORK

Sample	Initial			5 μgm. added			Recovery, %
	Reading	Blank	μgm./20 ml.	Reading	Blank	μgm./20 ml.	
Uncooked:							
1 (*a*)	15.0	4.0	2.75	35.0	4.0	7.75	100
1 (*b*)	15.0	4.0	2.75	35.0	4.0	7.75	100
2	9.75	3.0	1.69	29.75	3.0	6.69	100
3	18.25	5.5	3.19	37.5	5.5	8.00	96
4	17.5	5.25	3.06	37.5	5.25	8.06	100
5	16.5	3.5	3.25	35.5	3.5	8.00	95
Cooked:							
5	20.25	5.5	3.69	40.25	5.5	8.69	100
6	15.5	6.0	2.38	35.5	6.0	7.38	100
7	20.25	8.5	2.94	40.25	8.5	7.94	100

ethanol, and antimony trichloride – ethanol. The extract from 90 gm. was adjusted to pH 6.75 and made to a volume of 1200 ml. The following amounts of riboflavin: 0, 1.25, 2.5, 3.75, 5.0, 7.5, and 10.0 μgm., each contained in 5 ml. of water, were added to 20 ml. aliquots of the extract. Twenty-five millilitres of 95% ethanol was added to each, and, after centrifuging, fluorometric readings were made. In a second series, 25 ml. of 95% ethanol made to pH 2.62 with a few drops of concentrated hydrochloric acid was used. A third series employed 1 ml. of 1% antimony trichloride in absolute ethanol and 24 ml. of 95% ethanol (in combination these have a pH of 2.62) for precipitation. The hydrogen ion concentration of each series of clarified extracts was determined. A reference curve for acid ethanol proved to be the same as the curve for water. In Table III, the riboflavin contents of the initial aliquots have been calculated from reference curves for the appropriate solvents. In the same way, increments in fluorescence caused by added riboflavin have been calculated as recovered riboflavin. Recoveries were lower and the blank was slightly higher with ethanol clarification than with the other two treatments. Ethanol somewhat decreased the hydrogen ion concentration as well.

TABLE III

THE EFFECT OF THREE CLARIFICATION TREATMENTS UPON THE RECOVERY OF RIBOFLAVIN ADDED TO AN EXTRACT OF FRESH PORK

Treatment	Initial			Recovery, μgm./20 ml.						Average pH
	Reading	Blank	μgm./20 ml.	Added riboflavin						
				1.25	2.50	3.75	5.00	7.50	10.00	
Ethanol	15.5	3.5	2.40	1.00	2.25	3.25	4.70	7.10	9.65	6.90
Acid ethanol	15.5	3.0	3.13	1.25	2.50	3.75	5.00	7.50	10.00	6.75
Antimony trichloride ethanol	15.0	3.0	3.00	1.25	2.50	3.75	5.30	7.50	10.00	6.65

Since the antimony trichloride – ethanol precipitates appeared more dense, a test was made to determine whether this treatment precipitated more material from the extract than did the acid ethanol or ethanol. This was done by means of nitrogen determinations since the reaction of antimony trichloride with water to precipitate antimony trioxide (20, p. 473) precluded weighing. The precipitates from the foregoing experiment were pooled by treatments. Each combined precipitate was washed twice with 47.5% ethanol, dispersed in water, and made to 50 ml. Duplicate micro-Kjeldahl determinations were run on each as well as on a sample of the unprecipitated extract. The amount of nitrogen precipitated from the enzyme-hydrolysed pork extract was not great. Antimony trichloride – ethanol precipitated 4.0%, acid ethanol 3.4%, and ethanol 3.2% of the total nitrogen in the extract.

The antimony trichloride – ethanol procedure was used for the determination of riboflavin in four samples of fresh and four samples of cooked pork. Sampling and analyses were carried out in duplicate and the results compared with microbiological determinations on the same extracts. The means of duplicate determinations by the two methods were highly correlated ($r = .94$), as illustrated by Fig. 2A. The standard error of a single determination was ± 0 16 µgm. per gm. for the fluorometric method and ± 0 08 for the microbiological method. The standard error of prediction of the microbiological value from the fluorometric value was ± 0 19 for the means of the two determinations, and was only slightly greater than the expectation from the variance of duplicates alone. Twenty samples of cured pork, four cooked and 16 uncooked, were extracted and single determinations of riboflavin were made by both microbiological and antimony trichloride – ethanol methods. The correlation coefficient for the determinations by the two methods was 98 (Fig. 2B).

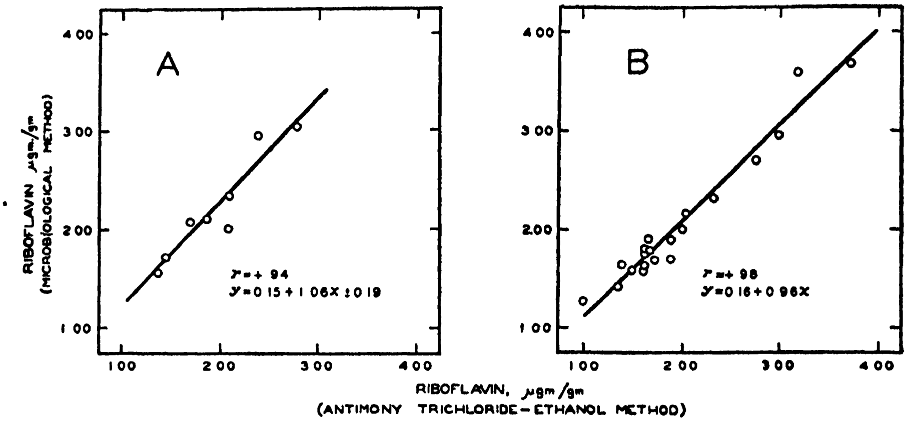

FIG 2 *Correlations of riboflavin determinations by the antimony trichloride - ethanol and microbiological methods All values calculated on fresh-weight basis*

A Means of duplicate determinations on fresh pork, uncooked and cooked.

B Single determinations on cured pork, uncooked and cooked

Discussion and Conclusions

Acetone and ethanol both intensify the fluorescence of riboflavin, so that the linear relations with concentration are different from the relation for water or antimony trichloride – ethanol (Fig. 1). Antimony trichloride in contact with water forms hydrochloric acid and a bulky white precipitate, antimony trioxide (20, p. 473). It is this hydrochloric acid that decreases the fluorescence of riboflavin in ethanol for the same reference curve as that for water was obtained when a few drops of concentrated hydrochloric acid were substituted for the trichloride.

Solvent precipitation as a means of removing interfering substances has been noted as untrustworthy (15) because riboflavin may become adsorbed on the precipitate. The fact that ethanol and acetone precipitation both gave results that were lower than those obtained microbiologically (Table I) tends to confirm this view. With antimony trichloride – ethanol precipitation, however, good agreement with microbiological assays (Fig. 2) and good recoveries of added riboflavin (Table II) were found. Low recoveries over a fairly wide range of concentration occurred when ethanol clarification was tested, but the addition of hydrochloric acid or antimony tricholoride to the ethanol resulted in almost perfect recoveries (Table III). This suggests that the presence of hydrochloric acid released by the antimony trichloride prevents the adsorption of riboflavin upon the precipitate.

It may be inferred from the good recoveries obtained using an external reference curve, that antimony trichloride – ethanol does not alter the fluorescence of riboflavin in pork extract. Therefore, an internal reference standard (6, 19, 22) with its more involved calculation is unnecessary. The external reference curve is so reproducible that routine calculations may be simplified further by multiplying the corrected readings by the factor 0.005 to convert them to concentrations in micrograms per millilitre.

In view of the high degree of correlation between microbiological and antimony trichloride – ethanol results, this method has been adopted by these laboratories for the routine assay of riboflavin in pork products.

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PRESERVATION OF EGGS

VI. EFFECT OF VARIOUS OILS AND OILING TEMPERATURES ON THE KEEPING QUALITY OF SHELL EGGS STORED AT 70° F. AND 30° F.[1]

By N. E. Gibbons,[2] Ruth V. Michael,[3] and Ursula Irish[3]

Abstract

The quality of eggs oiled when one day old with eight commercial oils and six mixtures and stored at 70° and 30° F. was assessed by candling, yolk index, and thick white height. Mineral oils with Saybolt viscosities of 70/100 at 100° F. maintained egg quality and prevented weight loss better than oils of lower viscosity. Viscosity of the oil seemed more important than pour point, although at 30° F. there was some indication that a high pour point was advantageous. Oiled eggs maintained their grades two to three times longer than unoiled eggs and lost from $\frac{1}{10}$ to $\frac{1}{2}$ as much weight. Heavy oil diluted with mineral spirits did not give as good results as lighter oils of comparable viscosity. The addition of vaseline and magnesium stearate improved the action of the light oils.

There was little difference in the quality of eggs dipped into oils maintained at 76°, 100°, and 130° F.

Introduction

In 1944 the British Ministry of Food requested the shipment of shell eggs to Britain and suggested that eggs placed in storage for shipment in the fall should be oiled. Although there are many reports on oils used for oiling eggs in the United States (e.g. 3, 6, 8, 9), little has been done in Canada. There is also some question as to whether the eggs should be oiled in cold or warm oil.* The present investigation was undertaken to determine which were the most suitable of the available oils and the effect of different temperatures of oiling.

Materials and Methods

The oils usually recommended for eggs are white mineral oils with low viscosities and high pour points. Oils of this type were obtained from a number of firms. Their characteristics as reported by the manufacturers, and as determined in these laboratories and by the N.R.C. oil testing laboratory, are given in Table I.

The main function of the oil is to seal the shell against water loss. The prevention of loss of carbon dioxide would also seem desirable so that the addition of substances more impervious to gas was indicated. Vaseline makes an excellent preservative but the thick films are messy and unsightly (7). In an attempt to seal the shell without the disadvantages of thick films one of the oils (*G*) was fortified with vaseline, or with magnesium stearate plus

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* *Shell Egg Committee of the Institute of American Poultry Industries. U.S. Egg & Poultry Mag. 48 : 302. 1942.*

TABLE I

PHYSICAL PROPERTIES OF OILS USED, ARRANGED IN ORDER OF DECREASING VISCOSITY

	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*
Laboratory findings								
Viscosity, Saybolt Universal sec., 100° F.[1]	100	89	81		60	59	52	51
Sp. gr., 60° F./60° F.	875	850	.847		.833	.833	.833	.830
Pour point, °F.	5	15	10		45	45	30	35
Flash point (O.C.), °F.	375	385	370		340	340	320	320
U.S.P. acid test	Fail	Pass	Pass	Pass	Fail		Pass	Pass
Viscosity, S.U. sec., 76° F.	168	120	109	98	79		64	63
100° F.	101	87	82	69	60		52	51
130° F.	76	63	60	55	50		44	44
Manufacturers' specifications								
Sp. gr., 60° F./60° F.		850/ 860	835/ 845	.835/850	825/ 840		820/.830	.825/.835
Viscosity, S.U. sec., 100° F.	77/82	85/90	70	70/80	50/60	50/60	50/60	50/55
Pour point, °F.	25	30	25	45	45	45	40	35
Flash point, °F.	355	345	310	345	325		300	280
Fire point, °F.	385	395	350	395	365			
Colour, Saybolt	30+	30+	30+	30+	30+		30+	30+

[1] *Calculated from centistokes.*

Nacconal. A heavy oil (350 viscosity) was diluted with an odourless kerosene in the proportions of 60:40 and 70:30. The viscosities of these mixtures are given in Table II.

TABLE II

SAYBOLT VISCOSITIES AT 76°, 100°, AND 130° F. OF THE OIL COMBINATIONS USED

—		Viscosity at:		
		76° F.	100° F.	130° F.
I	350 oil + kerosene 70 : 30	102	76	55
J	350 oil + kerosene 60 : 40	72	55	45
K	Oil *G* + 7% vaseline	69	58	46
L	Oil *G* + 5% vaseline	68	53	45
M	Oil *G* + 0.2% magnesium stearate + 0.015% Nacconal	66	53	44
N	Oil *G* + 0.3% magnesium stearate + 0.015% Nacconal	64	52	44

The eggs were obtained from one producer who maintains a large, well managed flock of White Leghorns to which no new blood has been added for a number of years. The eggs were gathered in the morning, cooled for a few hours, packed in new Keyes trays and cases, and shipped so as to arrive at the laboratory the next morning. On receipt, they were candled, and cracked and off-grade eggs discarded. The eggs had not been cleaned and some had small spots of faecal contamination; the most noticeable of these were brushed off. The majority of the eggs were large but some of medium size were distributed at random throughout the trays. Oiling was begun as soon as the eggs reached 50° F. to avoid surface moisture (dew point 45° F.). They were therefore oiled when one day old.

The oil was applied at the three temperatures commonly used; room temperature (in this case 76° F.), 100° F., and 130° F. The eggs were dipped into the oil for a few seconds, drained for approximately two minutes, and returned to the original trays.

The eggs were weighed in tray lots of 30 eggs in a clean tray before oiling, and after oiling and draining overnight, to determine the amount of oil retained on the shell. They were also weighed in lots of six for determination of weight loss.

Two lots of eggs were received and oiled on successive days. Those used as controls were not broken out until the day after the others had been oiled, i.e. they were two days old. Two dozen were examined from each lot and the average of these was taken as the initial value.

The eggs were stored in wooden export cases at 70° F. (21° C.) (about 40% R.H.*) and at 30° F. (−1.1° C.) (about 55% R.H.). The eggs stored at 70° F. were examined after 4, 6, 8, 10, and 12 weeks; those at 30° F. were examined after 8, 16, 24, 32, and 40 weeks.

At each sampling, one dozen eggs were removed, candled, and broken out on a glass plate to check quality. Egg quality was assessed by candling, the height of the thick albumen (10), the yolk index (5), and the pH of the mixed thick and thin white. The pH was measured with a Beckman pH meter and the instrument was frequently checked with a standard 7.8 buffer.

Results

Effect of Oils

At both storage temperatures candling results showed that the most noticeable effect of oiling was the prevention of evaporation. Usually the range allowed in the size of the air cell corresponds to the yolk shadow standards found in each grade (2). However, in oiled eggs evaporation was so slow that yolk shadow was the only criterion by which grade could be really assessed. At 70° F. control eggs had large air cells (Grade *C*) in six weeks whereas all oiled eggs at 10 weeks had air cells $\frac{3}{16}$ in. or less in height (Grade *A*). With some oils this still held true at 12 weeks. By this time eggs treated with the poorest oils and mixtures graded *B* on air cell size. In spite of the slight amount of evaporation, the yolk shadows became more distinct on storage. Most of the controls were graded *C* on yolk shadow at six weeks, whereas most of the oiled eggs were graded *A* and *B*. After 10 weeks' storage, the controls were 'no grade' and the oiled eggs were practically all Grade *C* on the basis of yolk shadow. Of the 504 oiled eggs examined after 12 weeks' storage only nine were classed as no grade before the lamp.

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* *R.H. = relative humidity.*

At the lower storage temperature the control eggs were graded *B* after 16 weeks' storage and *C* after 40 weeks. The majority of the oiled eggs were still Grade *A* after 32 weeks. At 40 weeks the air cells were on the border line between Grade *A* and *B* but based on yolk shadow most of the eggs were Grade *B*. Actually, of 504 eggs, 135 were graded as *A*, 362 as *B*, six as *C*, and one as no grade.

The value of oiling in maintaining quality at 70° F. is also apparent from the results presented in Table III. After 12 weeks the weight loss with the best oils (*A*, *B*, *C*, *D*) is $\frac{1}{10}$ or less of that of the unoiled controls while with the poorest oil it is $\frac{1}{4}$ of that of the controls. The yolk index (with the exception of Oil *G*) and white height after 12 weeks' storage is greater in the oiled eggs than in the controls after only four weeks' storage.

TABLE III

QUALITY TESTS ON OILED AND UNOILED EGGS AFTER 4 AND 12 WEEKS' STORAGE AT 70° F. AVERAGE VALUES PER EGG OVER THREE OILING TEMPERATURES. OILS ARRANGED IN ORDER OF DECREASING VISCOSITY

Oil	Weight loss, gm.		Yolk index		Thick white height, in.		pH	
	4 wk.	12 wk.	4 wk.	12 wk.	4 wk.	12 wk.	4 wk.	12 wk.
Unoiled[1]	3 64	11.80	.296	.174	.10	.08	9.29	9.30
A	0.29	1 00	394	.346	.18	16	8.36	8.20
B	0 38	0 87	.398	.357	.19	15	8 32	8.30
C	0 41	0 81	404	352	.18	16	8 30	8.25
D	0 22	1 05	.398	348	.19	.18	8 35	8.30
E	0 27	1 24	402	.343	18	16	8.40	8.48
F	0 40	1.14	400	.339	.18	15	8 34	8.39
G	0 41	2 70	.403	.281	.19	12	8 43	9.24
H	0 48	1.90	.396	.305	.18	.14	8 46	8.60
I	0.26	1 25	.415	.333	.19	.14	8.31	8.32
J	0.66	2 66	.410	.288	.18	.12	8 59	8 82
K	0 38	1 44	.406	336	.19	.16	8 40	8.64
L	0 40	1 46	.418	.337	.19	.15	8.36	8.62
M	0 39	1 56	403	.339	.20	.16	8 33	8 44
N	0 34	1 38	.407	.341	.19	.15	8.28	8.54
Necessary difference[2]	0 14		0 020		0 017		0.21	

[1] *Original values—yolk index, .454; thick white height, 0.26 in.; pH 8.68.*

[2] *Necessary difference applies to oiled eggs only.*

The original pH value is high as the eggs were not examined until the day after the others had been oiled. The true original value is probably between this value and that given for the oiled eggs at four weeks. With the poor oils (*G* and *H*), carbon dioxide was apparently lost throughout the test and the pH increased with time. In all of the others there seemed to be a retention of carbon dioxide and the pH decreased until the 8th or 10th week of storage and then increased.

The analysis of variance of these results (Table IV) indicates that most of the variance due to oils can be attributed to the poor oils and mixtures (*G*, *H*, *J*). Much of the remaining variance is no doubt due to Mixture *I*. From the necessary differences (Table III) it will be seen that when the above four oils are removed there is no significant difference between yolk indices with any of the other oils and little of significance with white height. With weight loss and pH the oils fall into two groups, Oils *A*, *B*, *C*, and *D* giving better results than the other oils and mixtures.

TABLE IV

ANALYSIS OF VARIANCE ON DATA FOR OILED EGGS ONLY, STORED AT 70° F.

Source of variance	Degrees of freedom	Weight loss, mean square	Yolk index, mean square	White height, mean square	Degrees of freedom	pH, mean square
Oils	13				13	
G, *H*, *J* vs. others	1	158,383**	21,249**	122 67**	1	29,544**
Residual	12	4513**	289*	2 60*	12	679**
Temperature of oiling	2	409	286	0 18	1	1585**
Storage time	4	77,055**	33,894**	109 83**	4	3774**
Oils × temp.	26	616**	275*	3 84**	13	184
G, *H*, *J* vs. others × temperature	2	270	53	5 30	1	55
Residual	24	645	293	3 72	12	195
Time × oils	52				52	
G, *H*, *J* vs. others × time	4	11,923**	2722**	9 74**	4	1305**
Residual	48	836**	192	1 67	48	294**
Time × temp.	8	384	397*	0 58	4	279
Oils × time × temp.	104	301	156	1 13	52	113

**Exceeds 5% level of statistical significance.*

***Exceeds 1% level of statistical significance.*

Heavy oil diluted with mineral spirits did not give as good results as the lighter oils of comparable viscosity. The addition of vaseline and magnesium stearate improved the action of the light oil used but not to the level of the better oils.

The results of storing at 30° F. are with few exceptions much the same as at the higher temperature (Table V). With Oil *C* there was a greater loss in weight between the 32nd and 40th week than was expected. This was noticeable in each of the three lots of eggs oiled at different temperatures. Oils *D*, *E*, and *F*, which have high pour points, preserved quality better at this temperature than at 70° F. Oil *H* was also much better at the lower temperature.

As at the higher temperature, the weight loss with the oiled eggs was from $\frac{1}{10}$ to $\frac{1}{4}$ of that of the controls. In all but two instances the total loss over 40 weeks of storage was less in the oiled eggs than in the control eggs after eight weeks. The yolk index and white height of the oiled eggs at 40

TABLE V

QUALITY TESTS ON OILED AND UNOILED EGGS AFTER 8, 24, AND 40 WEEKS AT 30° F.
AVERAGE VALUES PER EGG OVER THREE OILING TEMPERATURES.
OILS ARRANGED IN ORDER OF DECREASING VISCOSITY

Oil	Weight loss, gm.			Yolk index			Thick white height, in.			pH		
	8 wk	24 wk	40 wk	8 wk	24 wk	40 wk	8 wk	24 wk	40 wk	8 wk	24 wk	40 wk.
Unoiled[1]	1.46	4.27	7.20	440	404	390	21	20	20	8.86	8.88	9.01
A	0.07	0.43	0.71	456	449	441	22	20	21	8.12	8.06	8.29
B	0.23	0.42	0.77	449	457	437	23	21	20	8.00	8.04	8.30
C	0.22	0.50	1.11	452	439	435	23	21	20	8.14	8.10	8.25
D	0.14	0.55	0.95	451	451	414	23	21	21	7.98	7.98	8.56
E	0.21	0.47	0.84	479	444	444	24	22	22	8.24	7.98	8.22
F	0.18	0.44	0.77	439		431	22	20	21	8.04	8.02	8.06
G	0.25	0.87	1.73	442	437	407	22	20	19	8.21	8.44	8.70
H	0.11	0.52	0.89	456	438	450	23	20	22	8.22	8.26	8.30
I	0.19	0.96	1.04	457	430	413	23	21	21	8.20	8.22	8.35
J	0.25	1.29	1.66	447	418	416	23	19	21	8.32	8.68	8.60
K	0.11	0.41	0.71	442		434	23	21	23	8.12	8.22	8.21
L	0.18	0.42	0.90	446	453	439	23	21	23	8.11	8.19	8.32
M	0.19	0.45	1.04	457	444	429	24	24	23	8.14	7.96	8.46
N	0.13	0.56	0.84	434	444	429	23	21	21	8.02	8.24	8.38
Necessary difference[2]		0.17			0.016			0.02			0.16	

[1] *Original values—yolk index, 454, thick white height, 0.26 in.; pH 8.68.*
[2] *Necessary difference applies to oiled eggs only.*

weeks were as good as those of the unoiled eggs at 16 weeks. The final pH of all oiled eggs was much lower than that of the controls at eight weeks.

Effect of Oiling Temperature

During storage at 70° F. no significant effects of temperature of the oil at time of oiling could be found on white height, yolk index, or weight loss (Table IV). The pH was followed only in eggs oiled at 76° and 130° F.; eggs oiled at the lower temperature maintained a significantly lower pH throughout the storage period.

With eggs stored at 30° F. the temperature at which the oil was applied had no significant effect on weight loss, yolk index, or pH (Table VI). There was a significant effect with white height, the height being slightly lower in the eggs oiled at 76° F.

Amount of Oil Retained by the Eggs

The amount of oil retained by the eggs averaged from 1.0 to 2.4 gm. per tray of 30 eggs (each figure being the average of six trays), or 0.03 to 0.08 gm. of oil per egg. This is in agreement with Mallman's finding (6) of 0.06 to 0.07 gm. per egg. There was no apparent relation between amount of oil retained and the viscosity or temperature of the oil. It should be noted that these results were obtained after 24 hr. With the usual commercial equipment it has been found that it requires about twice as much oil having a viscosity of 70/90 as oil with a viscosity of 50/70. Warming the oil effects some saving.

TABLE VI

ANALYSIS OF VARIANCE ON OILED EGGS ONLY, STORED AT 30° F.

Sources of variance	Degrees of freedom	Weight loss, mean square	Yolk index, mean square	White height, mean square	Degrees of freedom	pH, mean square
Oils	13	6173.7**	666.8**	3.46**	13	1668.5**
Temp. of oiling	2	270.5	7.0	9.00**	1	236.0
Oils × temp.	26	160.2	152.9	1.65	13	71.2
Time	4	44,348.5**	3572.7**	26.50**	4	2622.0**
Oil × time	52	599.9**	271.5**	2.92**	52	286.5**
Temp. × time	8	130.2	131.0	3.63*	4	45.5
Oil × temp. × time	104	104.6	100.5	1.64	52	62.2

* *Exceeds 5% level of statistical significance.*
** *Exceeds 1% level of statistical significance.*

Discussion

The eggs used in this experiment were one day old when treated, which is said to be the ideal time for maintaining quality by oiling (4). The results indicate that oils with a Saybolt viscosity of 70 to 100 at 100° F. are more suitable for maintaining egg quality than the lighter oils. In general pour point was not as important as viscosity; at 30° F. however, a high pour point seemed to be of some advantage. The use of oil at temperatures higher than room temperature offered no advantage in preserving quality or in the amount of oil retained.

These findings are in the main in agreement with previous reports. Evans (3), using oils at about 70° F., found that those of higher viscosity preserved interior quality better than the less viscous ones. When applied at 239° F., oils with a viscosity of 134 Saybolt seconds were found to be more effective than those with a viscosity of 44 (1). Although in the present experiments the oils were used at much lower temperatures, the conclusions are similar. When a light oil was used, oiling at 60° F. was said to be better than oiling at 80° F. (9). The results presented here show that there was little difference between light and heavy oils applied over a much wider range of temperature. The use of oils at elevated temperatures seems to be a trade practice originating in a desire to save oil.

Although it seems reasonable that pour points above the storage temperature should give better results (8) the present work does not altogether support this claim. Some of the best oils had very low pour points according to the laboratory tests, and even according to the manufacturers' specifications the pour points were lower than the storage temperature. However oils with the same viscosity and different pour points were not available for comparison. Judging from the data presented in the above mentioned paper (8) there is an interrelation between viscosity and pour point.

Others (3) have noted that the reduction of the viscosity of an oil with solvents decreases its efficiency as an egg preservative; an oil having an original viscosity of 75 was diluted with 10% solvent to give a mixture with a viscosity of 58 to 62 Saybolt sec. at 100° F. The results were similar to those reported above (Table III, Oil *I*) when an oil with a viscosity of 350 was diluted to a final viscosity of 76.

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DRIED WHOLE EGG POWDER

XXIV. SOME FACTORS AFFECTING COLOUR[1]

By H. Tessier,[2] J. R. Marier,[3] and Jesse A. Pearce[4]

Abstract

A nine filter colour comparator was used to compare egg powders with strips showing the colour of dried egg as received in the United Kingdom. Drying either fresh or frozen eggs did not affect powder colour but Grade *B* and Grade *C* eggs gave a product with a more intense yellow colour than Grade *A* eggs. The area of Canada in which eggs were produced did not affect the colour of the subsequent powder appreciably but powders prepared from eggs produced in May to July, 1945 were a more intense yellow than those from eggs produced in January to April of the same year. Exposure of the liquid egg to light before drying resulted in powders of a duller grey colour than when the liquid was kept in the darkness. Commercial cone-type driers gave powders of a more intense yellow than commercial box-type driers, while powders prepared on the laboratory drier were paler than those prepared on the commercial driers. Coarse powders scattered less of the impinging light than fine powders but the colour quality of the scattered light was unaffected. The addition of a mixture of two dyes, Tartrazine and Sunset Yellow, to liquid egg before drying improved the colour of the resulting powder.

Introduction

Dried whole egg powder shipped from Canada to the United Kingdom was usually considered to be of excellent quality. However, a general complaint was made about the pale yellow colour of the powder and about a pinkish tinge that appeared in some powders. These complaints arise from differences in colour preferences of the people in the two countries. In England, an egg with a dark yellow yolk is usually preferred, while Canadians usually like an egg with a pale yolk. This and Canadian economics have led to the use of diets for Canadian egg layers that will produce a pale yolk, hence the undesirably pale colour of Canadian egg powder.

Although work in these laboratories (4) and elsewhere (2) had described the darkening that occurred in egg powder during storage, there was little information about other factors that may affect powder colour. Some of these, examined in the present study, are: the type of drier, the time of year and area of the country in which the eggs were produced, the quality of the eggs, and exposure of the liquid egg to light. In addition, powders containing added colouring were examined.

The present paper describes colour measurements on variously treated powders using a nine filter comparator designed in these laboratories (5). Description of the results was facilitated by referring the measurements to a

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set of coloured strips depicting the colour of egg powders received in the United Kingdom and kindly supplied by the Low Temperature Research Station at Cambridge, England.

Materials and Methods

Since the studies described here were diverse in nature, descriptions of the materials used will be given in the various subsections of the results.

Both the brightness or intensity and the chroma or colour quality of the samples were measured by a nine colour method used earlier for meat (5) and eggs (4). By this method, colour quality was determined as the light scattered by the sample within any one of nine colour bands (5). The light scattered in any one band is expressed as a fraction of the total light scattered by the sample in relation to the light scattered by the standard white surface of magnesium carbonate. The brightness of the sample was determined as an item separate from the analysis of colour quality.

Wherever possible, the colour data were treated by statistical methods, and the values for factors having no significant differences were grouped, averaged, compared with colour data for the Low Temperature Research Station (L.T.R.S.) coloured strips, and are recorded here in terms of these strips.

Results

Colour Analysis of Low Temperature Research Station's Coloured Strips

The slides submitted were divided into four groups or series: P_1 to P_3 represented pale, pinkish-coloured egg powders characteristic of some of the powder produced in Canada; $2Y_1$ to $2Y_5$ showed shades of yellow, typical of the normal range of colour in American samples; Y_1 to Y_5 resembled the $2Y$ series, but had a greyish-yellow appearance, and represented egg powders that had lost their lustre as a result of overheating during the drying process or because of poor storage conditions; and the slides in the B group extended the Y series and showed badly burnt powders. In each group the members with lower numbers were of a paler shade than those with higher numbers.

The results of brightness measurements on the foregoing strips are given in detail in Table I. These data show that the P series scattered the greatest amount of the impinging light, i.e. they were the brightest, and the B series scattered the least. The greyish Y series scattered less light than the pink P group but slightly more than the normally coloured $2Y$ slides. Within the various series, the members with higher numbers scattered less light than the members with lower numbers.

The results of colour quality measurements on the various slides are also given in detail in Table I. However, since these detailed data are difficult to visualize, the colour quality profiles showing the averages of values for each group are presented in Fig. 1. These profiles show that the pinkish P series scattered more light in the blue and blue-green regions of the spectrum (385 to 525 mμ) than any of the other series and that the normally coloured $2Y$

TABLE I

COLOUR ANALYSES OF LOW TEMPERATURE RESEARCH STATION'S COLOURED STRIPS DEPICTING EGG POWDERS AS RECEIVED IN THE UNITED KINGDOM

Strip number	Brightness, %	Colour quality, % scatter								
		Blue			Green			Red		
		385-434 mμ	434-458 mμ	458-487 mμ	487-525 mμ	525-556 mμ	556-584 mμ	584 614 mμ	614-644 mμ	Above 644 mμ
P_1	66 2	4 8	10 5	11 5	18 7	13 2	21 3	9 6	5 7	5 7
P_2	62 4	4 9	10 7	11 4	17 4	13 2	21 2	9 7	5 8	5 7
P_3	62 0	5 0	10 5	11 5	17 3	13 0	20 9	9 9	6 0	5 9
$2Y_1$	56 6	4 8	7 5	9 4	16 1	14 4	24 8	10 7	6 2	6 1
$2Y_2$	56 5	4 4	7 2	9 4	15 6	14 5	25 4	10 9	6 4	6 2
$2Y_3$	51 4	3 9	6 6	9 7	14 5	14 3	26 3	11 4	6 7	6 6
$2Y_4$	49 7	3 8	6 0	9 0	14 3	14 3	27 0	11 8	6 9	6 9
$2Y_5$	45 0	3 1	5 9	9 0	14 1	14 2	27 5	12 1	7 1	7 0
Y_1	59 4	3 9	8 3	10 5	17 2	13 8	23 5	10 3	6 2	6 3
Y_2	59 2	3 9	8 4	10 6	16 8	14 1	23 5	10 3	6 2	6 2
Y_3	56 2	3 7	8 0	10 3	16 5	13 8	23 9	10 7	6 4	6 7
Y_4	52 2	3 8	7 7	10 1	15 7	13 8	24 0	11 0	6 7	7 2
Y_5	51 4	3 5	7 5	10 4	15 5	13 3	24 0	11 3	7 0	7 5
B_1	43 6	2 8	7 6	9 9	15 2	13 4	24 1	11 6	7 2	8 2
B_2	43 4	3 2	7 5	10 4	15 6	13 1	23 7	11 4	7 1	8 0

group scattered more light in the yellow region of the spectrum (525 to 584 mμ). The greyish-yellow *Y* series showed a slight increase in scatter in the red region (above 644 mμ) and the burnt *B* series showed a marked increase in this region. The foregoing differences were generally accentuated by changes within the series, from the palest to the most intense shades (Table I).

These preliminary measurements provided a quantitative basis for the examination of some of the factors believed to be responsible for the pinkish colour of some Canadian egg powder. However, measurements necessitated the inclusion of a hypothetical coloured strip, which, from the values reported here, would be lettered $2Y_0$.

The Effect of Particle Size on Egg Powder Colour

Differences in colour were observed for powders prepared in commercial driers and in the laboratory drier (6) and these were attributed in part to differences in particle size. To clarify this point, eight samples of commercially produced egg powders were screened for one hour on a Ro-Tap rotary sifter using sieves of 35, 65, 80, 100, 120, 200, and 325 mesh (U.S. Bureau of Standards) and each fraction of the samples was examined for colour. The average colour profile for all samples and all mesh sizes matched the profile of the yellow 2*Y* series and in particular the $2Y_1$ strip. The major difference was in brightness: the coarse fractions scattered less light than the fine fractions (Table II*A*).

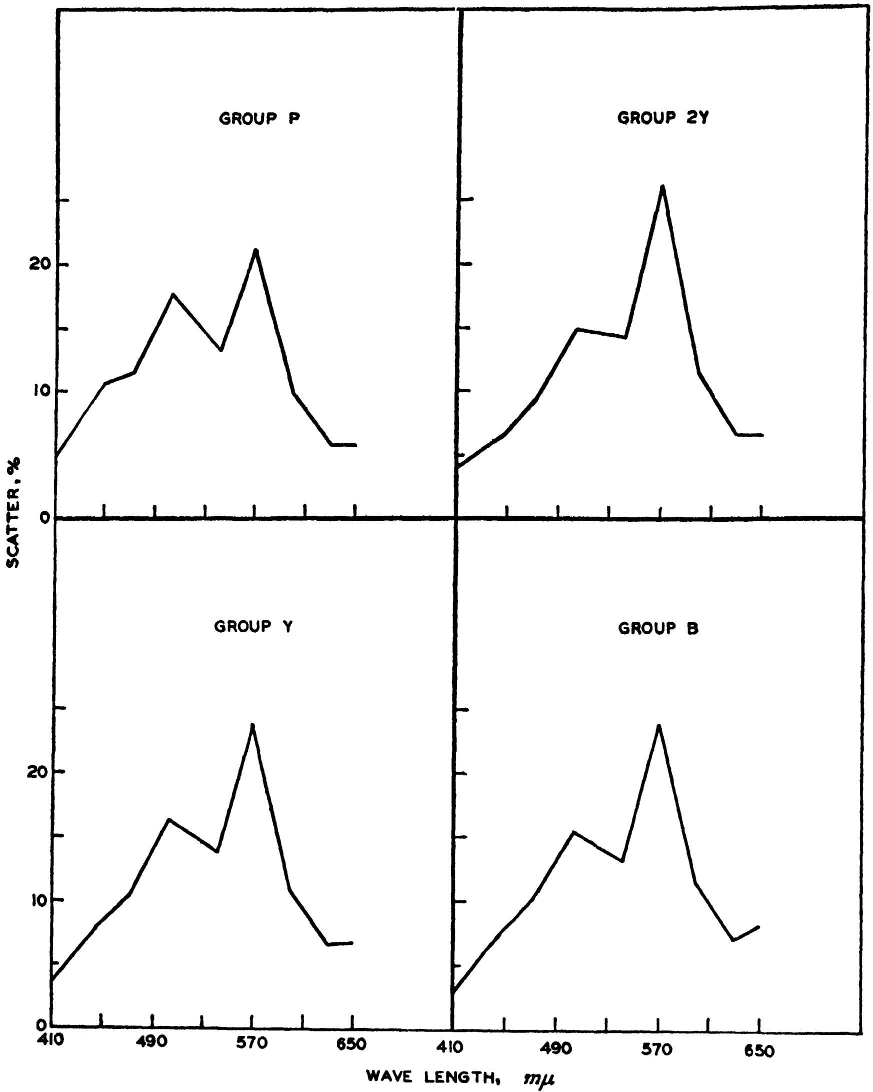

FIG. 1. *Colour quality profiles (averages) for the groups of coloured strips supplied by the Low Temperature Research Station, Cambridge, England.*

Sieving does not effect a complete separation of the particles of different sizes that are present in egg powder. Groups of particles may be seen in Fig. 2*e* at i, ii, and iii. These groups of particles do not break up during the sieving operation.

Further consideration was given to particle size and colour by the examination of powders prepared in a commercial cone-type drier using spray nozzles of different sizes: 0.065, 0.068, and 0.070 in. in diameter. The resulting powders matched the $2Y_1$ strip in colour distribution and, again, the finest powder (prepared using 0.065 in. nozzle) was the brightest (Table II*B*).

If the particle structure of egg powders is considered, explanation of the foregoing becomes apparent. Fig. 2 shows the microscopic structure of a number of samples. The particles passing a 35 mesh screen and retained by a 65 mesh screen are given for reference (Fig. 2*a*). These relatively large particles usually exude egg fat, which appears as smears (Fig. 2*a*) or discrete droplets (Fig. 2*f*). Powder from the main chamber usually consists of coarser particles than powder from the secondary chambers (Figs. 2*b*, 2*c*) and the difference between the main chamber and secondary chamber powder from cone-type driers is usually greater than the difference between the corresponding powders from the box-type driers.

TABLE II*A*

THE EFFECT OF PARTICLE FRACTIONATION BY SIEVING ON THE BRIGHTNESS OF EGG POWDERS

Particle range, U S Bureau Standards sizes	Brightness, % (average, eight samples)
35–65	49.1
65–80	52.1
80–100	51.8
100–200	53.3
200–325	55.9

TABLE II*B*

THE EFFECT OF SPRAY NOZZLE SIZE ON THE BRIGHTNESS AND PARTICLE SIZE OF EGG POWDERS PREPARED IN A CONE-TYPE COMMERCIAL DRIER

Nozzle diameter, in	Brightness, %	Average particle size, mm
0.065	56.0	0.03
0.068	54.2	0.05
0.070	51.5	0.4[1]

[1] *Size of clusters. Individual particles could not be measured*

The brightness differences recorded in Table II*B* are explained by Fig. 2 (*d*, *e*, *f*). Light is scattered from large particles in many directions and a relatively small proportion is reflected back to the light receptor (human or electric eye), while a powder made up of fine particles presents almost a plane surface and a greater amount of light is reflected in any one direction. From these considerations, and the data in Table I, fine powders should be paler in colour than coarse. The differences attributable to particle size would tend to weaken the comparison between brightness of powders and the brightness of the coloured strips. Nevertheless, it is believed necessary to give consideration to intensity measurements when transforming colour data to terms of the coloured stips.

Comparison of Canadian Egg Powder with L.T.R.S. Strips

It was thought desirable to determine how closely egg powder samples (commercial) could be matched with the various coloured strips by visual inspection, and opportunity was taken to determine whether the pinkish colour was attributable to the use of frozen liquid egg in the production of powder. As shown by the data in Table III, grading by visual examination gave a fairly good approximation of the results obtained by colour analysis. In addition, these results indicated that the use of frozen egg was not the sole cause of the pinkish powders.

TABLE III

COMPARISON OF METHODS OF CLASSIFYING EGG POWDER ACCORDING TO L.T.R.S. COLOURED STRIPS AND OF THE EFFECT OF THE PHYSICAL STATE OF THE EGG ON THE POWDER PRODUCED

Physical state of egg used to produce various powders	By colour analysis	By visual inspection
Shell eggs	$2Y_3$	$2Y_3$
Shell eggs	$2Y_0$[1]	P_1
Shell eggs	$2Y_2$	$2Y_2$
Shell eggs	$2Y_2$	$2Y_2$
Shell eggs	$2Y_2$	$2Y_1$
Mixed shell and frozen	P_3	P_2
Frozen melange	P_3	P_1
Frozen melange	P_3	P_3
Frozen melange	$2Y_3$	$2Y_2$
Frozen melange	$2Y_2$	$2Y_2$

[1] *This sample had the characteristics of the yellow 2 Y series, but the values matched those of a hypothetical strip in this series that would be numbered* $2Y_0$.

Colour Characteristics of Powders Prepared in Canadian Plants During Various Periods of the Year

Samples of powder were taken from both the main drying chambers and from the secondary collectors of various Canadian egg-drying plants at monthly intervals during the months of June to November, 1943 and in March, 1944. At that time, it was possible to obtain powder from five cone-type driers and from four box-type driers. Two of the box-type driers were rectangular in shape with flat bottoms and the other two had V-shaped bottoms. In general, fresh or stored shell eggs were processed during June, July, and August, frozen melange during September, October, and November and fresh shell eggs in March, 1944.

The results (Table IV*A*) showed that on the average all powders collected from the main chambers of the various driers corresponded to the yellow 2 *Y* group of slides and that the powders from the cone-type and V-bottom, box-type driers were more intensely coloured than the powders from the flat-bottom box. The powders from the secondary collectors of the cone-type drier were burnt more than the powders from the secondary collectors of the

PLATE I

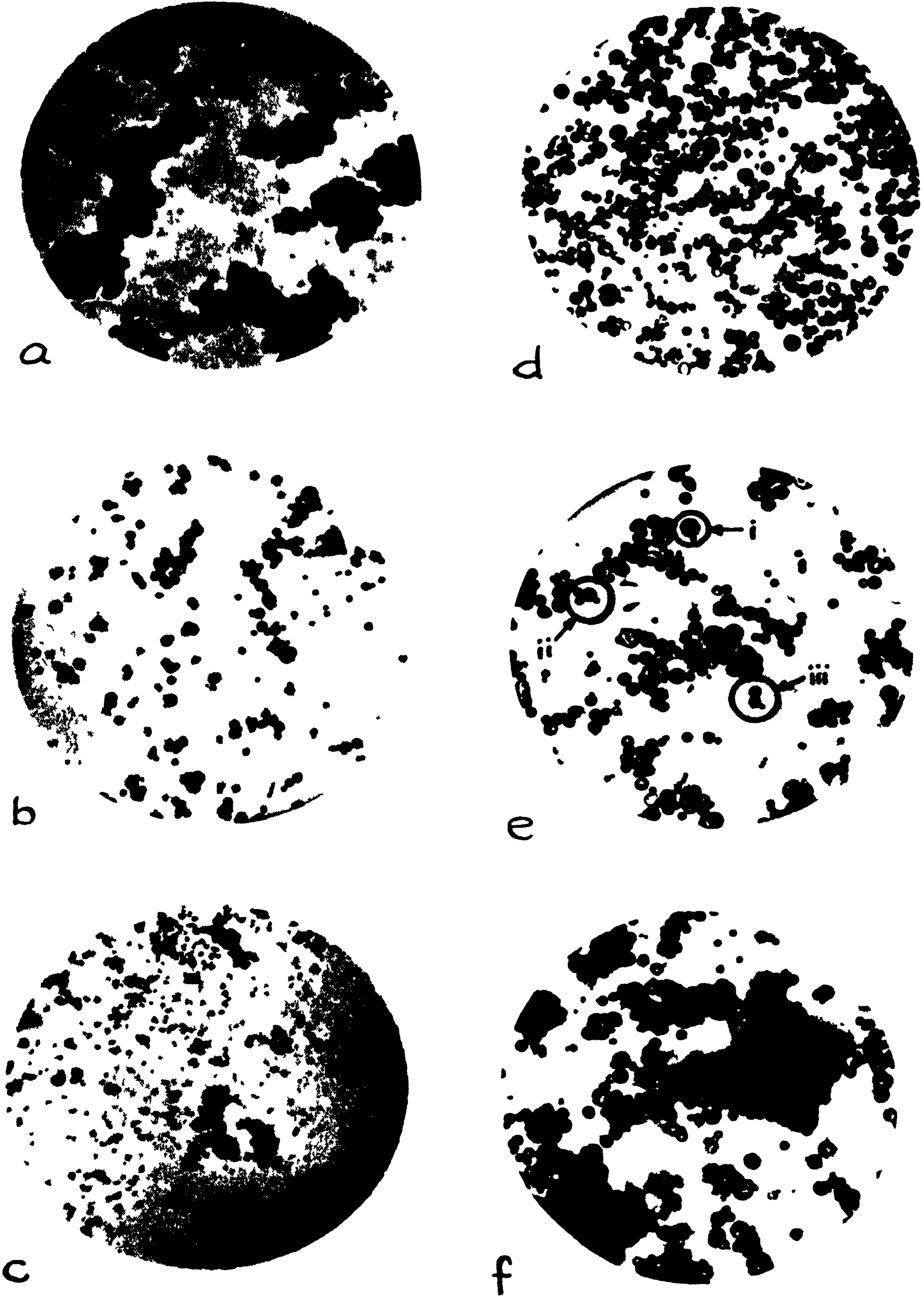

FIG. 2 *Photomicrographs of egg powder (× 37)*

(a). Fraction of a powder passing a 35 mesh screen and retained by a 65 mesh screen (U. S. Bureau of Standards)

(b) Powder from the main collector of a flat bottomed, box type drier

(c). Powder from the secondary collector of a flat bottomed, box type drier

(d), (e), and (f) Powders from the main collector of a cone-type drier, prepared using nozzles 0.065, 0.068, and 0.070 in. in diameter, respectively

TABLE IV*A*

EFFECT OF DRIER TYPE AND COLLECTION CHAMBER ON THE COLOUR OF COMMERCIALLY PREPARED EGG POWDER

Type of driers	Number in operation	Grade according to L.T.R.S coloured strips	
		Main chamber	Secondary collectors
Box, flat-bottom	2	$2Y_1$	Y_1
Box, V-bottom	2	$2Y_3$	Y_4
Cone	5	$2Y_4$	B_1

other two types. Since the powder caught in the secondary collector is finer than the powder trapped in the main chambers, it is reasonable to expect that these particles had dried faster and hence were more likely to be burnt.

Only the powder prepared in March, 1944 differed from the other powders (Table IV*B*). This supported previous evidence that the use of frozen egg had little effect on the colour of powder, but indicated that the time of year during which eggs are produced may have a pronounced effect.

TABLE IV*B*

EFFECT OF MONTH OF PRODUCTION ON THE COLOUR OF COMMERCIALLY PREPARED EGG POWDER COLLECTED FROM THE MAIN DRYING CHAMBERS OF NINE DRIERS

Month of production	Grade according to L.T.R.S coloured strips
June to November, 1943	$2Y_3$
March, 1944	Y_3

Colour of Powders Prepared in a Laboratory Drier and in Commercial Driers

The survey of powders prepared in various commercial plants indicated that season of production of the eggs may be an important factor affecting the colour of egg powder. Information about this point could best be obtained by using the laboratory spray drier (6); therefore, a comparison was made of the differences in the colour of powder prepared in the laboratory drier and in commercial driers. For this purpose, two lots of frozen melange were used: a portion of one lot processed in western Canada was dried in a V-bottom, box-type drier and another portion in the laboratory drier; and a portion of the second lot processed in eastern Canada was dried in a cone-type drier and a portion in the laboratory drier.

As seen in Table V, the laboratory drier gave normally coloured powders ($2Y$ series) but these powders were a paler yellow than the powders from the commercial driers. This may have been a function of the scale of the laboratory and commercial operations: egg is dried in the laboratory drier at lower temperatures than in commercial operations. In addition, this study indicated that the region of the country in which the eggs were produced might also affect the colour.

TABLE V

COLOUR OF EGG POWDERS PREPARED IN COMMERCIAL DRIERS AND IN A LABORATORY DRIER

Source of frozen melange	Type of drier	Grade according to L T R S coloured strips
Western Canada	Laboratory	$2Y_0$[1]
	Commercial, box-type, V-bottom	$2Y_1$
Eastern Canada	Laboratory	$2Y_1$
	Commercial, cone type	$2Y_3$

[1] *See Table III*

The Effect of Grade of Eggs and Locality and Month of Production on the Colour of the Resulting Powder

A comprehensive study was made of the effects of grade of eggs and the month and locality of egg production on the quality of the powder produced and these results have been reported (3). Colour measurements, made on the same material, are presented here. In brief, the experimental design required shipments of Grade *A** (large, medium, and pullet), Grade *B*, and Grade *C* eggs from Vancouver, Edmonton, Winnipeg, London, Belleville, and Three Rivers on the 15th of each month from December, 1944 to July, 1945. Upon receipt in the laboratory the various samples of eggs were dried in the laboratory drier, and therefore, all the colours recorded here are somewhat paler than would be obtained in a commercial drier.

The area of production had no significant effect on the colour of powder prepared from Grade *A* eggs; the averages of the colour measurements showed that eggs from all areas corresponded to the hypothetical colour strip $2Y_0$, i.e. a very pale powder of a normal yellow shade. It was not possible to get Grade *B* eggs from the Vancouver area, but a comparison for the other five areas showed that Grade *B* eggs from Edmonton, Winnipeg, and London gave powders corresponding to the yellow $2Y_2$ strip while a similar grade of eggs from Belleville and Three Rivers gave powders corresponding to the paler $2Y_1$ strip. In general, powders from Grade *B* eggs were a more intense yellow than powders from Grade *A* eggs. Unfortunately, insufficient Grade *C* eggs were received to make a valid comparison of these and Grades *A* and *B* eggs for the various areas.

When considering the effect of month of egg production, a marked difference was observed between powders prepared from eggs produced between January and April and those produced between May and July. The data for this period were, therefore, subjected to further mathematical analysis (Grade *C* eggs were included in these considerations). The results in Table VI show that eggs produced in the early part of the year, while still of a yellow colour, were much paler than eggs produced later in the year and Grade *C* eggs gave a more intensely coloured powder than Grade *B* eggs, which, in turn, were a more intense yellow than Grade *A* eggs.

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* *Descriptions of the various grades of eggs can be found in (1).*

TABLE VI

COLOUR OF POWDERS PREPARED FROM EGGS OF DIFFERENT QUALITY PRODUCED DURING JANUARY TO APRIL AND MAY TO JULY, 1946

Grade of eggs	Period of production	Grade according to L T R S coloured strips
A	Jan to Apr	$2Y_0$[1]
	May to July	$2Y_1$
B	Jan to Apr	$2Y_2$
	May to July	$2Y_4$
C	Jan to Apr	$2Y_2$
	May to July	$2Y_5$

[1] *See Table III*

The differences attributable to grades of eggs can be explained on the basis of the Canadian grading system (1) When candled, the yolks of Grade *A* eggs must be barely discernible, the yolks of Grade *B* eggs can be somewhat darker, and the yolks of Grade *C* eggs can be distinctly visible and even mottled. The seasonal differences are probably a reflection of the onset of warm weather and the corresponding transfer of hens from buildings to out-of-doors.

Effect of Sunlight and Ultra-violet Light on the Colour of Egg Powder

The drying described in the previous section was usually done in a fairly well lighted laboratory. During the work, it was observed that samples prepared on a cloudy day were slightly different from samples prepared on a sunny day. Therefore, an examination was made of powders prepared from liquid egg exposed to sunlight or to an ultra-violet light (carbon arc) or from liquid held in total darkness Powder prepared from liquid exposed to the ultra-violet light had the greyish tinge common to strips in the *Y* series and corresponded to strip Y_3 while powder from liquid exposed to sunlight corresponded to the normal yellow strips and matched $2Y_3$. Powder from liquid egg held in total darkness was unlike any of the L.T.R S. strips. The colour quality of this powder when compared with the colour quality of the $2Y$ group (Fig. 1) showed greater scatter in the yellow region of the spectrum (556 to 584 mμ) and reduced scatter in the blue–green region (487 to 525 mμ).

This powder should represent a third group of strips of a more brilliant yellow than any forwarded from England and should be represented by a series called 3*Y*.

The Effect of Added Colouring Matter on the Colour of Egg Powder

Since alteration of the foregoing factors would effect little improvement in the colour of egg powder, it was thought possible that a more desirable looking dried egg powder might be prepared by the addition of various colouring materials. For this purpose, the dye combinations listed in Table VII were added in various amounts to liquid egg before drying in the laboratory spray-drier. Of these, none gave a powder with a colour profile similar to any of the series shown in Fig. 1, and many powders were so badly coloured that they were undesirable. Colours approximating the yellow 2*Y* series, by visual inspection, were obtained by the use of: 4 ml. of cheese colouring; 10 ml. of pie colouring (5% solution); or 5 ml. of a mixture of 9 parts Tartrazine and 1 part Sunset Yellow (5% solution) per litre of liquid egg. Considerations of cost and ease of handling led to the selection of the Tartrazine – Sunset Yellow mixture. By colour analysis, powders containing this dye scattered less light in the blue region of the spectrum (385 to 487 mμ), and more in the blue-green (487 to 525 mμ) and in the red (584 to 644 mμ) regions than the desirable yellow 2*Y* series. However, these powders met the visual requirements and commercial scale, trial shipments to the United Kingdom had a satisfactory colour.

TABLE VII

Dyes[1]	Proportions	Amounts, ml., added to one litre of liquid egg
Cheese colouring[2]	—	0 5, 1, 2, 4
Lemon pie colouring[3]	—	5, 10, 20
Tartrazine[4]	-	5, 10, 20
Tartrazine : Ponceau[4]	3 1	10
Tartrazine : Sunset Yellow[4]	3 : 1	10
Tartrazine : Sunset Yellow	7 . 1	5, 10
Tartrazine : Sunset Yellow	9 : 1	5

[1] *All but cheese colouring consisted of 5 gm. solid made up to 100 ml. with water: cheese colouring concentration was unknown.*

[2] *Kindly supplied by Chateau Cheese Co., Ottawa, Ont.*

[3] *Kindly supplied by Canadian Doughnut Co., Trenton, Ont.*

[4] *Kindly supplied by Dye and Chemical Co. of Canada, Ltd., Kingston, Ont.*

Acknowledgments

The authors wish to express their thanks to Dr. J. W. Hopkins for statistical advice and to Mr. W. R. Coutts who made the statistical computations.

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DRIED WHOLE EGG POWDER

XXV. FURTHER STUDIES ON THE EFFECT OF ADDED SUBSTANCES[1]

By R. L. Hay,[2] Margaret Reid,[2] and Jesse A. Pearce[2]

Abstract

A number of substances added to liquid egg before drying had no effect on changes in palatability, fluorescence value, and total carotinoid pigment content of the subsequent powders when stored for 16 weeks at 80° F., for eight weeks at 100° F., or for four weeks at 120° F. Added soya lecithin did not increase the initial fluorescence, but egg lecithin did; added lecithin from either source did not accelerate fluorescence changes during storage. Measurement of vitamin A content in treated or untreated powder showed that loss of this component during four weeks' storage at 120° F. was less marked than during 16 weeks' storage at 80° and 100° F., but, at these lower temperatures, heated whole egg powder, heated dried white, heated dried yolk, and heated or unheated cystine or methionine had a preservative action. Sucrose or sodium bicarbonate retarded vitamin A loss in stored dried yolk. Foaming volume measurements on freshly dried powders containing Nacconol S.N.F., Duponol, Roccal, and Aerosol showed that, in general, the addition of these wetting agents to liquid egg before drying adversely affected the aerating power of the powder. The addition of sucrose improved the baking quality of freshly prepared powders, the addition of lactose had a negligible effect and the addition of whey solids reduced the baking quality. When the powders were stored at 80° and 100° F. these three added substances had a preservative effect; sucrose being most effective and whey solids least effective.

Introduction

Dried egg deteriorates during storage even at moisture and temperature levels well below those currently in use by commercial egg drying establishments. As a result, several studies have appeared on the use of added substances in retarding deterioration (1, 9, 12, 15). Previous work in these laboratories showed that sucrose or sodium bicarbonate, when added to whole egg before drying, were effective in retarding loss in quality during subsequent storage (4, 12). Stored egg powder containing lactose has been found to have greater foaming power than a similar powder containing the same concentration of sucrose (2). The addition of 10% of spray-dried whey (containing about 70% lactose) to egg liquid prior to drying had the same protective effect as the addition of 10% lactose when the powders were stored at 117° F. (2).

Other substances likely to affect the keeping qualities of egg powder during drying and storage were indicated by work in related fields. Calcium acid phosphate and phenyl mercuric nitrate offered points of theoretical interest—the phosphate because of its use in baking, and the nitrate because it is believed to react with sulphur-containing compounds. If the sulphur-containing groups were involved in fluorescence development in egg powder,

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it was thought that their combination with a mercuric compound might prevent development of fluorescing substances. Lecithin, a component of egg commonly believed to be responsible for the development of off-flavours in many food products, may have been responsible for fluorescence increases in stored egg powder and thus warranted study. Since the previously noted (12) beneficial effect of sodium bicarbonate might be attributable to the presence of the carbonate ion, it was also believed advisable to ascertain whether carbon dioxide added before or during drying would retard fluorescence changes in stored powders.

During preliminary work (11) using a model spray drier (16) it had been observed that excessive heating during the drying operation seemed to prevent loss (oxidation) of vitamin A content in stored egg powder. Since this antioxidant action may have been caused by changes in the sulphur-containing amino acids, added cystine or methionine might prevent excessive loss of vitamin A in stored egg powder.

Reconstituted dried egg is seriously deficient in foaming power. It was believed that wetting agents, if their presence did not accelerate deterioration, might facilitate the reconstitution of egg powder and thus increase the foaming power.

The present paper amplifies some of the foregoing observations by describing: the changes in palatability and fluorescence of stored egg powders containing substances likely to affect deterioration of quality; the changes in vitamin A content of stored dried egg containing substances with possible antioxidant effect; the effect of wetting agents on the foaming power of egg powder; the changes in the baking quality of egg powders containing various amounts of sucrose, lactose, and whey; and the effects of sucrose or sodium bicarbonate on dried yolk or dried white.

Materials and Analytical Methods

All egg powders used in the investigation were prepared in a laboratory spray drier (16) at an inlet temperature of 250° F. and an outlet temperature of 140° F. and were adjusted to final moisture contents between 2 and 3%. Substances under study were added to the liquid egg before drying.

Palatability was assessed by a panel of 14 people, who tasted each sample as scrambled egg. The procedures used for reconstituting the powder and for scoring were the same as those described in an earlier publication (10).

A previously described procedure (10) for measuring fluorescence was used throughout, with the exception that a greater number of defatting operations was necessary to remove all the fat from the dried yolk.

The procedure used for measuring total carotinoid pigments provided a rough arbitrary evaluation of the amounts present in the powder (14). One gram of dried whole egg powder was weighed on an analytical balance to 5 mgm. The sample was transferred to a 250 ml. Erlenmeyer flask and 100 ml. of redistilled acetone was added. The flasks were corked tightly and the mixture was gently swirled intermittently for 10 min. The mixture was then poured into an 18-cm. No. 12 Whatman folded filter paper and the filtrate collected in a narrow-necked glass vessel, which was tightly corked immediately and kept closed until needed. The transmission of this filtrate was measured, at 444 and 465 mμ on a Lumetron Colorimeter using matched square cuvettes. Redistilled acetone was used as the standard of 100% transmission.

Vitamin A estimation was done by a method outlined by Dann and Evelyn (3). The L values in Table V are for the total blue colour produced by each sample, no correction being applied for any remaining carotinoid pigments.

Foaming volume has been found suitable, with reservations, as a measure of the baking quality of egg powder (4, 7, 13). The foaming volumes of some unstored powders were determined by two procedures: in the first, 40.5 gm. of powder was mixed thoroughly with 75 ml. of distilled water and then beaten for 10 min. in a 'Mixmaster', set at No. 10 speed; the second eliminated the variable egg solids – added substances ratio, unavoidable in the first method, and maintained the egg solids in each determination at 19 gm. The foam was measured in a graduated cylinder. Foaming volumes of the stored powders containing added carbohydrates were measured using the first procedure.

The baking quality of some of the stored egg powders was also evaluated by measuring the volume of sponge cakes prepared by a procedure described in a previous publication (7).

Results

Effects of Added Substances on Changes in Quality and Carotinoid Pigments of Whole Egg Powder

This portion of the study evaluated the effect of materials added to the liquid egg before drying on changes in palatability, fluorescence, total carotinoid pigments, and vitamin A content of stored egg powder. The materials added and the concentrations used are given in Tables I and III. Carbon dioxide was added in unknown concentration but was introduced in two ways; in the first, the melange was saturated with the gas shortly before drying; in the second, the carbon dioxide was introduced into the drier during the drying process. The dried products were stored in tin-plate (air as headspace gas) for 16 weeks at 80° F., eight weeks at 100° F., and four weeks at 120° F. The times for this exploratory work were chosen on the basis of work described in earlier papers and permitted examination of the powders at about the point where they became unsuitable for use as an egg dish. Carotinoid and vitamin A determinations were not done on samples stored for eight weeks at 100° F. but were done on samples held for 16 weeks at this temperature.

As shown in Table I, the added substances used caused no significant change in the eating quality of fresh or stored whole egg powders as assessed by either fluorescence or palatability measurements.

The deteriorative changes in dried egg during storage may be due to the reaction of reducing sugar with amino acids (1, 6, 8). Sulphur-containing

TABLE I

EFFECT OF VARIOUS ADDED SUBSTANCES ON THE FLUORESCENCE AND PALATABILITY CHANGES IN STORED WHOLE EGG POWDER

Treatment of liquid whole egg	Fluorescence value				Palatability	
	Initial	80° F., 16 weeks	100° F., 8 weeks	120° F., 4 weeks	Initial	80° F., 16 weeks
Untreated	15 0	47 4	58 0	84 3	8 0	6.6
Liquid egg saturated with CO_2	13 2	40 1	60 1	86 0	8.0	6.6
CO_2 introduced into air in drier	12 0	47 1	65 0	85 0	7.7	6.0
Whole egg powder, 0.1%[1]	13 0	46 1	65 0	88 0	8.1	6.0
Dried white, 0 1%[1]	13 5	44 4	56 0	74.4	8 0	6.3
Dried yolk, 0 1%[1]	12 9	43 1	61 2	82 0	7 9	6.8
Cystine, 0 005%	14 4	46 0	59 2	81 4	8 1	6 6
Cystine, 0 005%[1]	12 1	43 1	55 3	76 0	8 5	6.0
Methionine, 0 005%	14 1	42 3	58 2	78 1	8 5	5 6
Methionine, 0 005%[1]	14 0	42 0	55 0	68 1	8.1	6.0
Nacconal S.N.F , 0 02%	15 1	41 0	59 3	86 1	7.6	7.0
Duponol, 0 02%	14 0	37 4	57 0	79 4	7 5	6 5
Phenyl mercuric nitrate, 0 08%	13 2	42 1	60 3	85 0	—	—
$CaHPO_4$, 0 2%	12 5	47 3	67 3	82 1	8 5	6.9

[1] *Heated for one hour in a vacuum oven at 212° F.*

amino acids may be involved in this reaction as it progresses in egg powder (6), however phenyl mercuric nitrate did not prevent their action nor did the addition of methionine or cystine increase the fluorescence values. This sugar–protein reaction produces some carbon dioxide (6). The beneficial effect of this gas or of the carbonate ion in preserving stored egg powders (9, 12) may, therefore, be explained by the law of mass action. The negligible effect of carbon dioxide in the present experiment is probably due to failure to attain a sufficiently high concentration in the powder.

The addition of lecithin as a possible cause of fluorescence development was given more detailed study. Commercially available egg and soya lecithin were compared by adding them to different lots of liquid egg at levels of 0, 0.01, 0.1, and 1.0%. In addition, some of each of the lecithins was heated for one hour in a vacuum oven at 212° F. before being added to different lots of liquid egg at the 1% level. The powders containing lecithin and a control sample were held at 80° and 100° F. and the fluorescence was determined initially and after one-, two-, three-, four-, and five-week periods. Since it was difficult to attain homogeneity in the liquid, the fluorescence values were more variable than usual. Therefore the data were subjected to an analysis of variance; the results are shown in Table II. As might be expected, both time and temperature had a significant effect on fluorescence development. From the results in Table II the necessary difference for significance* was calculated, and the samples that did not differ were grouped and averaged. The average values for the groups are given in Fig. 1. Neither heated nor

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* *5% Level of statistical significance.*

TABLE II

ANALYSIS OF VARIANCE ON FLUORESCENCE DATA FROM A STORAGE EXPERIMENT ON EGG POWDERS WITH OR WITHOUT ADDED EGG LECITHIN OR SOYA LECITHIN

Variance attributable to:	Degrees of freedom	Mean square
Samples	8	254**
Temperature	1	4013**
Time	5	1674**
Samples × temperature	8	9
Samples × time	40	13
Temperature × time	5	280**
Residual (Error)	40	11

** *Surpasses 1% level of statistical significance.*

TABLE III*A*

EFFECT OF ADDED SUBSTANCES ON THE TOTAL CAROTINOID PIGMENTS OF STORED WHOLE EGG POWDER

Treatment of liquid whole egg	Transmission,[1] %							
	Filter 444 mμ				Filter 465 mμ			
	Initial	80° F., 16 weeks	100° F., 16 weeks	120° F., 4 weeks	Initial	80° F., 16 weeks	100° F., 16 weeks	120° F., 4 weeks
Untreated	89.6	90.1	93.0	93.2	89.4	88.6	93.7	94.4
Whole egg powder, 0.1%[2]	84.7	88.3	93.0	89.7	87.0	85.2	91.0	91.5
Dried white, 0.1%[2]	81.1	82.2	86.5	86.0	82.4	81.8	82.2	90.3
Dried yolk, 0.1%[2]	75.3	74.5	82.5	84.4	76.8	79.1	81.1	86.6
Cystine, 0.005%	82.3	81.6	85.2	85.6	81.3	83.1	87.0	90.5
Cystine, 0.005%[2]	73.0	74.6	81.4	82.0	74.5	76.6	82.4	84.7
Methionine, 0.005%	76.0	76.9	81.6	81.5	77.4	77.8	84.3	85.6
Methionine, 0.005%[2]	81.5	74.4	82.2	89.3	82.5	82.3	85.2	90.3

TABLE III*B*

EFFECT OF VARIOUS SUBSTANCES ON THE VITAMIN A CONTENT OF STORED WHOLE EGG POWDER

Treatment of liquid whole egg	L value[3]			
	Initial	80° F., 16 weeks	100° F., 16 weeks	120° F., 4 weeks
Untreated	20.2	10.6	7.9	22.4
Whole egg powder, 0.1%[2]	17.8	14.1	10.6	14.7
Dried white, 0.1%[2]	22.4	16.7	18.7	17.5
Dried yolk, 0.1%[2]	17.4	16.4	18.7	17.5
Cystine, 0.005%	19.3	14.1	13.8	18.2
Cystine, 0.005%[2]	19.9	16.0	14.9	19.2
Methionine, 0.005%	16.3	18.7	10.6	17.8
Methionine, 0.005%[2]	18.8	13.8	12.0	16.2

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[1] *Varies inversely as the carotinoid pigment content.*

[2] *Heated for one hour in a vacuum oven at 212° F.*

[3] *Varies directly as the vitamin A content.*

unheated soya lecithin affected the initial fluorescence value of the powder but unheated egg lecithin caused a slight increase and heated egg lecithin caused a marked increase in the initial fluorescence value. However, the addition of lecithin did not accelerate fluorescence development during storage.

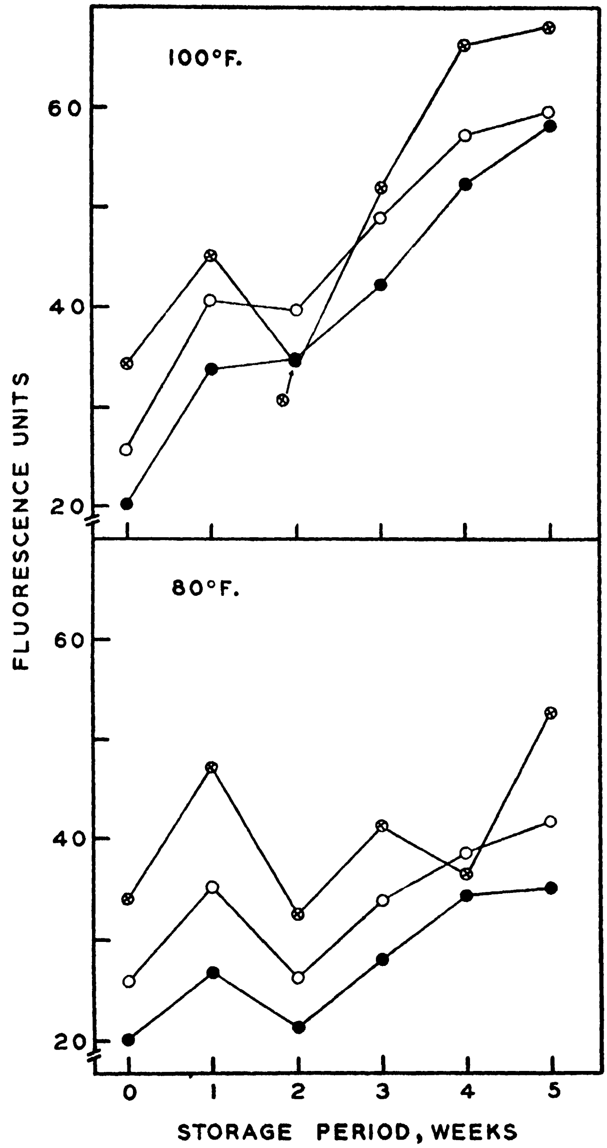

FIG. 1. *The effect of added heated or unheated egg or soya lecithin on the fluorescence changes in stored egg powder.*

● *Control powders and powders containing heated or unheated soya lecithin.*
○ *Powders containing unheated egg lecithin.*
⊕ *Powders containing heated egg lecithin.*

The results in Table III*A*, based on transmission values that vary inversely as the carotinoid content, show that most of the materials, studied primarily for their antioxidant effect, had no significant effect on changes in total carotinoid pigments. This may be partly attributable to wide variation in carotinoid pigments in the freshly prepared powders. Little change occurred during 16 weeks at 80° F. but reduction in carotinoid pigment was noticeable in all samples after 16 weeks at 100° F. and after four weeks at 120° F.

As shown in Table III*B*, all of the addition substances examined in this phase of the investigation (heated whole egg powder, heated dried white, heated dried yolk, and heated or unheated cystine or methionine) had a beneficial effect on vitamin A retention during storage at 80° and 100° F. No significant reduction in vitamin A content was observed in treated or untreated whole egg after four weeks at 120° F. After 16 weeks at 80° or 100° F. the loss of vitamin A was considerable. Previous work showed that loss of vitamin A was pronounced at all storage temperatures from 15° to 100° F. (5).

Effects of Sodium Bicarbonate and Sucrose on Changes in Dried Egg White and Dried Egg Yolk

Further information about the manner in which sucrose or sodium bicarbonate exert a beneficial effect on whole egg was sought by examination of dried white and dried yolk containing these substances. Sodium bicarbonate effectively retarded fluorescence changes in egg white stored at 120° F. and accelerated fluorescence development at 80° and 100° F. (Table IV*A*). This compound was mildly effective in inhibiting fluorescence development in yolk stored at 100° and 120° F. but had no effect at 80° F. Sucrose accelerated deterioration in yolk but had no determinable effect on the white. These and former observations (12) indicate that bicarbonate is most effective in retarding fluorescence development at high storage temperatures. From the data in Table IV*A* and previous work (2, 12) it appears that sucrose is not an effective preservative of eating quality unless used in dried whole egg. These problems are receiving further attention in the laboratories.

As shown in Table IV*B*, the presence of sodium bicarbonate had no effect on total carotinoid pigments in dried yolk. The large quantity of added sucrose diluted the carotinoid pigment content as measured but also appeared to reduce the change during storage. Loss in vitamin A content of yolk was marked under all conditions of study but reduction was retarded noticeably by the presence of sucrose (Table IV*C*).

Effects of Added Wetting Agents on Foaming Volume of Whole Egg Powder

Since wetting agents did not accelerate deterioration, their effect on the foaming power of reconstituted egg was evaluated by adding the following to the mélange prior to drying: Nacconol S.N.F., Duponol, Roccal, and Aerosol.

TABLE IV

EFFECT OF SODIUM BICARBONATE AND SUCROSE ON CHANGES IN STORED DRIED WHITE AND STORED DRIED YOLK

A. Fluorescence value

Treatment of liquid white or yolk	Fluorescence value			
	Initial	80° F., 16 weeks	100° F., 8 weeks	120° F., 4 weeks
White				
Untreated	8.0	41.1	68.0	165.0
Sodium bicarbonate, 0.2%	8.0	66.1	164.0	46.0
Sucrose, 15%	11.7	40.0	86.0	158.0
Yolk				
Untreated	15.0	52.2	57.0	54.0
Sodium bicarbonate, 0.2%	14.0	56.0	48.1	43.0
Sucrose, 15%	10.5	64.0	97.2	165.0

B. Carotinoid content

Treatment of liquid yolk	Transmission, %							
	Filter 444 mμ				Filter 465 mμ			
	Initial	80° F., 16 weeks	100° F., 16 weeks	120° F., 4 weeks	Initial	80° F., 16 weeks	100° F., 16 weeks	120° F., 4 weeks
Untreated	80.1	80.0	86.0	87.0	81.5	81.2	87.1	89.6
Sodium bicarbonate, 0.2%	80.1	82.1	83.5	88.0	81.5	81.0	88.7	90.2
Sucrose, 15%	95.1	95.5	96.8	98.0	95.5	94.5	97.8	99.7

C. Vitamin A content

Treatment of liquid yolk	L value			
	Initial	80° F., 16 weeks	100° F., 16 weeks	120°F., 4 weeks
Untreated	30.7	18.7	18.7	19.2
Sodium bicarbonate, 0.2%	26.2	21.1	14.9	18.7
Sucrose, 15%	22.4	20.3	16.4	21.4

Table V shows that the presence of wetting agents usually had an adverse effect on the foaming volume of plain egg powder. Although powders containing 0.01, 0.02, or 0.04% Duponol had higher foaming volumes than plain egg powder, similar amounts of added Nacconol, Roccal, and Aerosol had either a negligible or a detrimental effect. For all powders containing higher quantities of wetting agents the foaming volumes were lower than for untreated powders.

TABLE V

EFFECT OF ADDITION OF WETTING AGENTS ON FOAMING VOLUME OF WHOLE EGG POWDER

Concentration of wetting agent, %	Foaming volume, ml.			
	Nacconol	Duponol	Roccal	Aerosol
0	323	323	323	323
0.01	324	356	314	326
0.02	312	368	321	330
0.04	279	349	303	322
0.08	286	264	301	310
0.20	269	298	298	272
0.50	271	258	279	263

Effects of Added Sucrose, Lactose, and Whey on Foaming Volume and Baking Quality

Samples of egg powder containing 0, 3, 6, 9, 12, 15, or 18% sucrose, lactose, or whey solids were prepared. Some samples were examined for foaming power and baking quality before storage while others were sealed in air and stored at 80° and 100° F. Samples were examined by foaming volume only after four weeks' storage at 80° F. and after two weeks' storage at 100° F. At about this time, it became apparent that foaming volume was not a satisfactory measure of baking quality and the final testing, after 12 weeks' storage at 80° F. and eight weeks at 100° F. was for baking volume only.

Two procedures for foaming volume were used since it was difficult to add either carbohydrate or egg in such a way that all components would have identical prior treatment. The results obtained using both foaming volume procedures were similar in nature and are presented graphically in Fig. 2. In subsequent work only the procedure based on a constant amount of total solids in the mix was used.

Fig. 2 shows that the higher quantities of added sucrose resulted in a product with much greater foaming volume than that of untreated powders. Large quantities of lactose had practically no effect and large quantities of whey solids affected foaming volume adversely. It was also noted that powders containing 12% or more whey solids had an offensive odour that might prove harmful to the palatability of baked products.

Results after storage (Fig. 3) showed that, in addition to having the best initial foaming volumes, sucrose treated powders were most stable in this attribute during storage at 80° and 100° F. for four and two weeks respectively. Further examination by baking volume measurements (Fig. 3) also showed the marked beneficial effect of added sucrose on the baking quality of fresh and stored powders. Contrary to the results observed with the foaming

Page 168, first line of paragraph under subheading under Table V for "0,3,6,9,12,15, or 18%" read "0,10,20,25,30,35, or 40%".

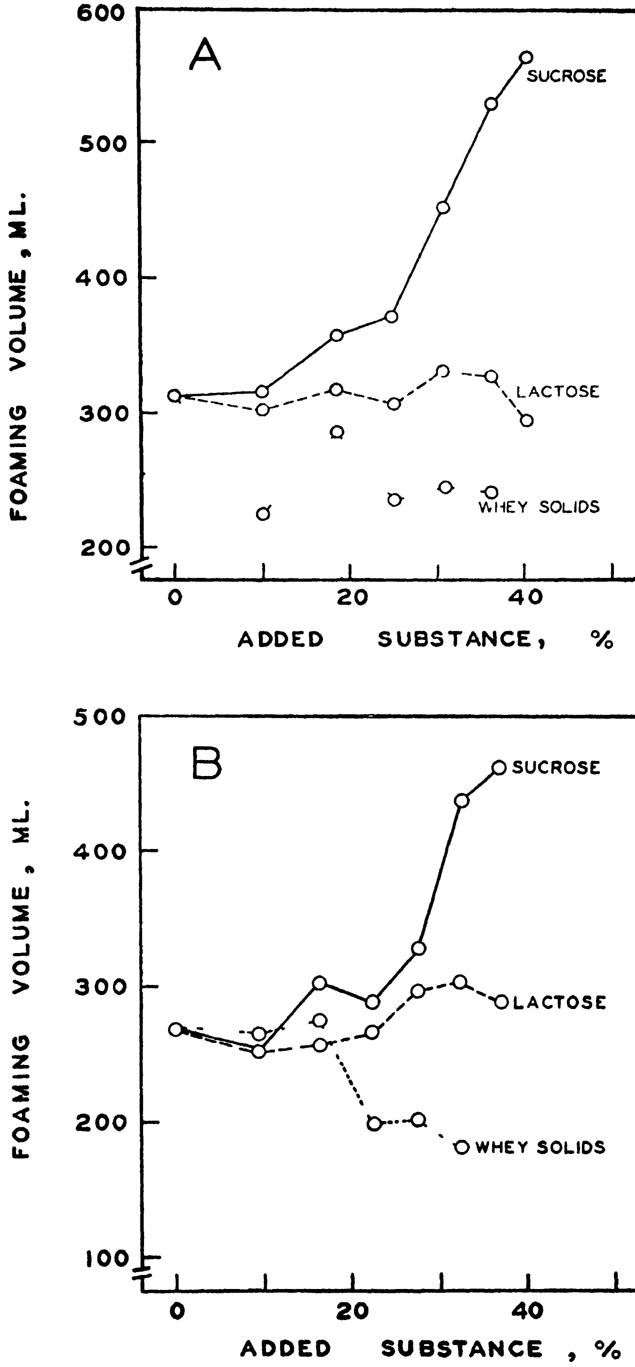

FIG. 2. *The effect of added sucrose, lactose, and whey solids on the foaming volume of egg powder; A, total solids in the mix are kept constant; B, egg solids in the mix are kept constant.*

volumes, lactose improved the baking quality of the fresh powders and provided some protection to stored powders. Added whey had an adverse effect on the baking volume of freshly prepared powder but retarded changes in the stored powders.

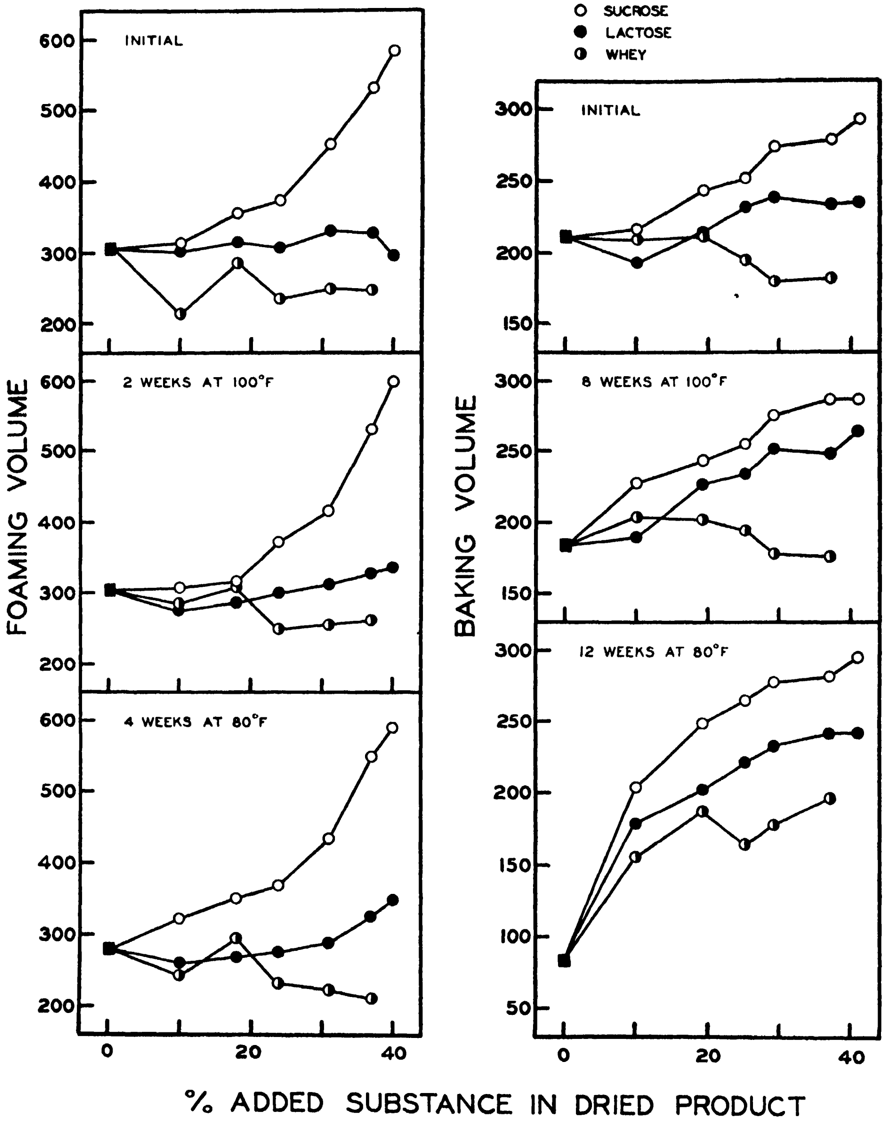

FIG. 3. *The effect of added sucrose, lactose, and whey solids on the foaming volume (total solids in the mix are kept constant) and baking quality of stored egg powder.*

The marked protective action (in terms of aerating power) provided by sucrose, a non-reducing sugar, and the lesser protective action of lactose, a reducing sugar, when considered in relation to the sugar–protein reaction is at present unexplainable. This is receiving further attention in these laboratories.

Foaming Volume and Baking Quality of Mixtures of Dried Whole Egg and Dried Whey

To test the effect on foaming volume of whey added to whole egg powder, 0, 10, 20, 30, or 40 gm. of dried British or Canadian whey solids was mixed with 19 gm. of plain egg powder, 56 ml. of water was added, and the mixture was beaten and measured in the usual manner. The resulting foaming volumes, given in Table VI*A*, indicated that sponge cakes prepared from egg powder with part of the sucrose replaced by whey would be lower in volume than cakes produced from dried egg and sucrose.

TABLE VI

FOAMING VOLUME AND BAKING QUALITY OF MIXTURES OF DRIED WHOLE EGG AND DRIED WHEY

A. Foaming volume

Amount (gm.) of dried whey added to 19 gm. of whole egg powder	Foaming volume, ml.	
	Canadian dried whey	British dried whey
0	186	180
10	160	148
20	154	114
30	137	104
40	121	101

B. Baking quality

Weight (gm.) of sugar in baking formula replaced by British dried whey	Baking volume, ml.
0	209
1	210
3	182
7	126
15	93

To verify this, 0, 1, 3, 7, or 15 gm. of spray-dried British whey was mixed with 6 gm. of plain egg powder and sucrose was added to make the whey and sucrose for each determination total 20 gm. The solids were mixed thoroughly with 19 ml. of tap water, followed by beating for 10 min. in a 'Mixmaster' set at No. 10 speed. Then 20 gm. of standardized super cake flour was incorporated with the least amount of mixing. The remaining portion of the baking procedure used here was the same as that described previously (7). The volumes of sponge cakes made using these mixtures are given in Table

VI*B* and confirmed the above indication that the volume of sponge cakes prepared by substituting dried whey for sucrose decreased as the amount of added whey increased.

Acknowledgments

The authors wish to express their thanks to Canadian Industries Limited who kindly supplied the Duponol used in this investigation, to Miss S. Jegard, Biochemist, who measured the baking volumes, and to Messrs. H. Tessier and G. A. Young, Laboratory Stewards, for their valuable technical assistance.

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DRIED WHOLE EGG POWDER

XXVI. SOME OBSERVATIONS ON THE QUALITY OF POWDER PREPARED FROM FROZEN, LIQUID EGG[1]

By Jesse A. Pearce,[2] H. Tessier,[3] C. G. Lavers,[4] and M. W. Thistle[2]

Abstract

Liquid from eggs of various qualities was frozen at −40° F. and stored at 10°, 0°, and −10° F. for 12 months. Powder produced from the defrosted samples was assessed by fluorescence and potassium chloride solution solubility measurements, which showed that liquid from musty or incubator reject eggs gave a less desirable powder than liquid from Grade *A*, Grade *C*, or cracked eggs, increase in time of frozen storage decreased the quality of the resulting powder, if frozen storage extended beyond six months, the lowest storage temperature was most desirable, and method of packaging (in Reynold's Metal A-10, or in wax paper with or without added ice) had no effect on the quality of the powder produced. If drying conditions were held constant, increased dilution of the defrosted egg before drying resulted in a poorer powder. It was shown that freezing or defrosting operations should be completed within about one hour.

Introduction

At the time these studies were planned, it was apparent that large quantities of the eggs produced in the spring and summer in Canada and used for subsequent drying would have to be stored. The capacity of the drying equipment available was not sufficient to process during the flush season the total amount of powder required for export, nor even to process the eggs within the time they might reasonably be stored in the shell. Eggs in the shell should be held for no longer than about three months and conditions required that they be held for six to eight months. This long term holding is usually done by breaking the eggs, mixing the white and yolk, and freezing the resulting liquid. However, little information was available to describe the effects of frozen storage of liquid egg on the quality of the resulting powder. This paper describes the results of quality measurements on powder produced from frozen liquid egg.

Materials and Methods

The material used in the preliminary study was prepared from the meats of Grade *A* large, fresh eggs. For this study, 700 ml. aliquots of egg were frozen into blocks 5 × 7 × 1.5 in. at −40° F. The blocks were lashed together in sets of four, separated by wooden strips so that each block had an equal area of surface exposed. The sets were stored unwrapped for 18 months at 0° and 15° F.: some exposed to the air in the storage rooms; others in closed

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desiccators containing 50% and 20% sulphuric acid. Initially, the acid solutions should have given relative humidities of 35% and 87%, but these values no doubt changed slightly until equilibrium was reached.

The later more comprehensive storage study utilized material described in earlier papers (2, 5). In brief, liquid from fresh Grade *A* eggs, from Grade *A* eggs held for 16 hr. at 80° F. in sterile glass containers, from Grade *C* eggs, from cracked eggs, from musty eggs, and from 'eight-day' incubator reject eggs was poured into moulds containing about four litres, frozen within 16 hr. in a room operating at $-40°$ F., and held at temperatures of 10° ($+ 2°$, $- \frac{1}{2}°$), 0° ($\pm$ 1°) and $-10°$ ($\pm$ 1°) F. for a period of one year. Samples were dried before and after freezing and after 3, 6, and 12 months' storage. The liquid from fresh Grade *A* eggs was packed in Reynold's Metal A-10, a highly moisture vapour resistant material (8), plus a Fourdrinier Kraft, B-Flute carton; in wax paper (40 lb. Kraft, waxed to 50 lb.) plus the carton, with ice cubes inside the carton and surrounding the wrapped egg; and in wax paper and carton without added ice. All the other samples were packed in Reynold's Metal A-10 and cartons.

Accessory studies on material prepared from the meats of Grade *A* large, fresh eggs included evaluation of the effects of dilution of the defrosted egg, freezing rates, and defrosting rates. The freezing time was considered as the time for the centre of the block to reach a temperature of $-20°$ F. At this temperature approximately 7% of the melange is still unfrozen (6).

The egg was dried in a laboratory spray drier (10), and for all but the freshly frozen material, the inlet and outlet temperatures were 250° and 140° F. respectively. Dilution of defrosted egg is usually desirable if the viscosity of the material is to be reduced to a point where the egg can be handled by the pump on the drier and was a necessity when using the laboratory drier. In an attempt to keep the dilution constant, the defrosted egg used in the storage study was dried after addition of an equal volume of water. This effected an excessive reduction in the viscosity of freshly frozen egg and, to obtain a dry powder, less material could be put through the drier with a corresponding increase in outlet temperatures (150° to 155° F.). However, it was possible from previously available data, some of which have been published (9), to correct the values for the analytical measurements on these samples to values that would be expected at 140° F., thus bringing all measurements to a reasonably comparable basis.

The quality of the powder was assessed by measurements of fluorescence and potassium chloride solution solubility values (4, 7).

Results

The results of the preliminary experiment are given in Table I. When thawed, most of the samples were viscous and had to be diluted before they would flow through the pump and the drier nozzle: the proportions of added water are shown in the table. It appeared from the analytical measurements

TABLE I

EFFECT OF TEMPERATURE AND HUMIDITY ON FROZEN EGG STORED 18 MONTHS BEFORE DRYING

(Drying conditions: inlet temp. 250° F.; outlet temp. 140° F.)

Storage conditions		Dilution necessary for drying, egg : water	Quality of resulting powder	
Temp., ° F.	Relative humidity, %		Fluorescence value	Potassium chloride value
0	Room	1 : 1	25.6	57
	35	2 : 1	19.5	62
	87	2 : 1	19.6	62
15	Room	1 : 1	25.2	65
	35	2 : 1	24.6	61
	87	Undiluted	21.7	63
Unfrozen egg		Undiluted	18.0	73

that prolonged frozen storage had an adverse effect on solubility as assessed by potassium chloride values, and on eating quality as assessed by fluorescence measurements. There was some evidence that a storage temperature of 0° F. was preferable to 15° F. Greatest deterioration seemed to occur in the samples exposed to the room air, but this may have been attributable to the large quantity of water added before drying.

Since dilution may have affected powder quality, it seemed desirable to consider this factor before proceeding to the next phase of the investigation. The results of drying defrosted egg mixed with different quantities of water (Table II) indicated that dilution does affect fluorescence values adversely, but some dilution was necessary if solubility was to be retained. Diluting

TABLE II

EFFECT OF DILUTION OF THAWED FROZEN EGG ON THE QUALITY OF POWDER PRODUCED

(Drying conditions: inlet temp. 250° F.; outlet temp. 140° F.
Egg defrosted at 40° F.; time, 48 hr.)

Dilution, egg : water	Fluorescence value	Potassium chloride value
Unfrozen egg		
No dilution	18.9	83.2
5 : 1	21.7	80.0
1 : 1	22.3	78.8
Freshly frozen egg		
No dilution	18.0	67.1
20 : 1	19.0	78.4
7 : 1	26.6	75.4
4 : 1	25.3	73.6
1 : 1	28.5	71.7

fresh liquid egg had only a slight effect on the quality of the subsequent powder. The adverse effects can be partially eliminated if the pump rate is kept constant and the outlet temperature is allowed to vary according to the amount of water present (1). After these trials, it was believed that, to obtain comparable results in subsequent experimental work, the defrosted egg should be diluted with the same proportion of water.

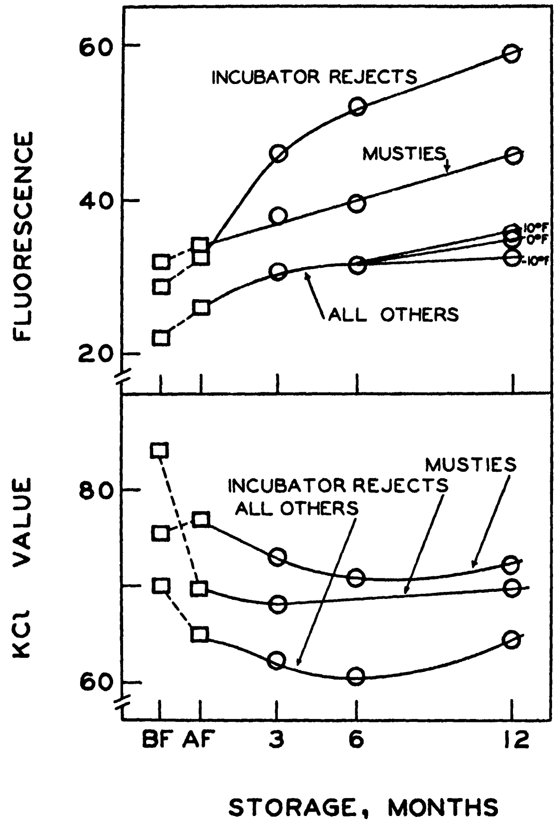

Fig. 1. *The effect of freezing and frozen storage of liquid egg on the quality of powder produced.*

Defrosting temperature, 40° F., time 48 hr.

Dilution: one part of defrosted egg to one part water, by volume.

Drying conditions: inlet temp., 250° F.; outlet temperature, 140° F.; except for material dried just after freezing.

B.F.: before freezing; A.F.: after freezing.

The results of the more comprehensive storage experiment are shown in Fig. 1. Since many of the factors studied had no effect on the quality of the powder, measurements to assess these factors were considered as replicates and average values are shown in the figure.

Powders prepared from frozen incubator rejects and musty eggs were definitely of poor quality as assessed by the fluorescence measurement.

However, the solubility of these powders was better than that of powders from Grade *A*, Grade *C*, or cracked eggs. It is possible that enzymic digestion of the protein occurred in the incubator reject and musty eggs and that these processes made the protein fraction more soluble in potassium chloride solution. Failure to differentiate between powders from Grade *A* and Grade *C* or cracked eggs may be attributable to the limited number of samples used or to the changes occurring during freezing Previous work has shown that Grade

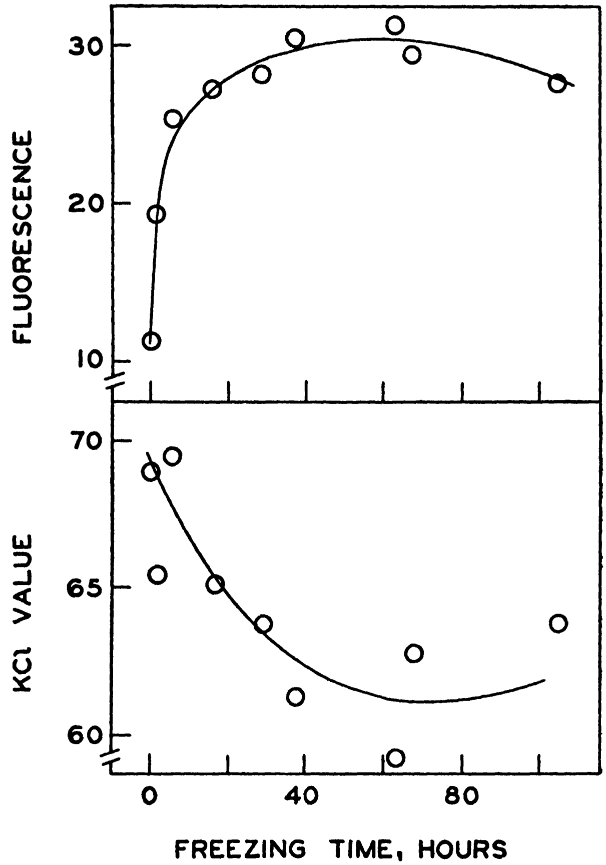

FIG 2 *The effect of the rate of freezing liquid egg on the quality of the powder produced Defrosting temperature, 40° F, time, 48 hr*
Dilution one part defrosted egg to one part water, by volume
Drying conditions inlet temp, 250° F, outlet temperature, 140° F

C eggs produce a less desirable powder than Grade *A* eggs (3), and the present experiment indicated that freezing liquid from Grade *A* eggs reduced the quality below that of unfrozen Grade *C* eggs

The three methods of packaging frozen eggs had no effect on the quality of the powder, and the storage temperatures used affected only the fluorescence values of powder produced from egg stored for 12 months The values obtained indicated that storage at −10° F. was preferable, and that there was little difference between temperatures of 0° and + 10° F.

Storage time had a greater effect on the fluorescence values than on the potassium chloride values, although in general, the latter measurements showed a marked loss in solubility as a result of the freezing operation: this decrease in solubility has also been observed in commercial practice. The fluorescence values were slightly greater than those encountered in commercial practice and in the preliminary study. It was believed that these high values may have been attributable to freezing or defrosting techniques. These techniques were subjected to further examination.

Egg is usually frozen commercially in 30- or 40-lb. lots and the operation requires from 24 to 72 hr. depending on the method used. In the preliminary experiment, the small blocks of egg used were frozen within a few hours while in the later experiment a much longer time was required. The results of an experiment to evaluate the effect of freezing rates on the quality of the resultant powder are given in Fig. 2 and show that the quality of the powder becomes progressively poorer as the freezing time is increased from 1 to 20 hr., but that further increase in freezing time had little effect on quality.

In commercial practice, frozen egg is usually pulverized or broken into small fragments that may be mixed with water or fresh egg liquid. The temperature of these liquids is not allowed to exceed 45° F. and defrosting is usually completed in one to four hours. In the preliminary experiment, defrosting was done in water at 100° F. and completed rapidly, but in the later experiment defrosting was done at 40° F. and required about 48 hr. The results in Table III show that rapid defrosting provided a liquid from which an excellent powder could be produced and that long defrosting times gave powders with high fluorescence values. The solubility of the product was affected by other

TABLE III

EFFECT OF DEFROSTING TEMPERATURE AND TIME ON THE QUALITY OF POWDER PRODUCED FROM FROZEN LIQUID EGG

(Liquid brought to 40° F.; 15% water added; and dried at inlet temp. of 250° F. and outlet temp. of 140° F.)

Defrosting		Fluorescence value	Potassium chloride value
Temp., ° F.	Time, hr. (approx.)		
100[1]	1	18.9	78.6
80	10	22.0	72.5
70	18	20.6	74.8
60	28	22.6	70.4
50	40	23.8	73.8
40	48	29.0	76.3

[1] *With stirring and container in contact with water; all others without stirring and containers in contact with air.*

factors since high solubilities were obtained from both the most rapidly and the least rapidly defrosted egg.

The foregoing results indicate that frozen egg can be used to produce powder of a satisfactory quality. However, the frozen egg should be stored no longer than six months at temperatures of 10° and 0° (if a longer storage time is necessary, storage temperature should be −10° F.); should be frozen and defrosted in a minimum time, preferably about one hour for each operation; and should have the least possible water added when reducing the viscosity for spraying into the drier.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XX. INFLUENCE OF THE INOCULUM ON THE *AEROBACILLUS POLYMYXA* FERMENTATION[1]

By A. C. Blackwood[2] and G. A. Ledingham[3]

Abstract

Whole wheat fermentations were started with known numbers of *Aerobacillus polymyxa* in the range from 50 thousand to 4000 million per ml. of mash. Increasing the initial numbers of the bacteria decreased the lag phase and increased the maximum numbers obtained. Although the initial rate of fermentation was increased, all the fermentations were finished at the same time and gave similar yields of 2,3-butanediol.

The effects of added nutrients, incubation temperature, aeration, and reduced pressure on bacterial growth in the inoculum media were investigated but none of the treatments used had an appreciable effect on the subsequent fermentation. The use of a backstocking technique appears to be a practical method of inoculation.

Introduction

Although certain factors affecting the inoculum in connection with the *Aerobacillus polymyxa* fermentation for the production of *l*-2,3-butanediol have previously been investigated in these laboratories (7, 9), pilot plant operations have shown the necessity for a more detailed study of this problem. It has been found (8) that biotin and a number of amino acids are essential for the growth of this organism and that yeast extract supplies these necessary factors. In a study of various nutrient supplements for starch fermentation by *A. polymyxa*, Fratkin and Adams (4) found that malt sprouts were the most effective. Aeration and reducing the pressure on the fermenting medium were found to increase the fermentation rate and affect the yield of products (1, 2).

The purpose of this investigation is to relate the nutrition and treatment of the inoculum to the actual growth of the culture and to assess the effect of this growth on the production of 2,3-butanediol. The effects of temperature, aeration, reduced pressure, and nutrilites on the inoculum and the effect of the amount of inoculum added and of 'backstocking' on the fermentation have been assessed in comparative experiments.

Materials and Methods

The *Aerobacillus polymyxa* strain used in these experiments was previously isolated in this laboratory and is designated as C3 (2). Stock cultures were carried on wheat agar medium at 30° C.

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The procedures used in preparing inoculum mash (5% finely ground whole wheat or 2.75% commercial starch) and fermentation mash (15% ground whole wheat) have been described previously (9). Three hundred millilitres of fermentation mash in a 500-ml. Erlenmeyer flask was used except in the studies of the effects of amount of inoculum and reduced pressure on the fermentation. In the latter studies it was desirable to remove samples at definite intervals from the fermentation medium without appreciably affecting the surface volume ratio, thus 2.5-litre bottles containing 1 litre of mash were used.

In laboratory practice it has been customary to add a 24-hr. inoculum equal to 3.0% of the volume of the mash. In all experiments designed to test the effects of added nutrient or treated inoculum, both 3 0% and 0 1% additions were studied.

The number of organisms was determined either by the direct count method using a Petroff-Hauser plate or by the standard plating technique. The results given are averages of duplicate tests. Difficulties were encountered with the plate method because of a tendency of the colonies to spread rapidly and though less tedious than the direct count method, dilutions must be made immediately and the results are not available at once. The direct count was used in most cases.

All fermentations were carried out in duplicate. Where 2,3-butanediol analysis was desirable at 48 and 72 hr., four flasks were incubated for each set of conditions and two removed at each time As fermentation conditions were constant throughout in most experiments only 2,3-butanediol was estimated as an indication of inoculum effect on product yield. In those experiments where the inoculum was aerated or subjected to reduced pressure both 2,3-butanediol and ethanol were determined The analytical methods employed for the determination of 2,3-butanediol and ethanol have been described elsewhere (9) All analyses were done in duplicate and averages are reported. Microscopic examinations and pH determinations were carried out on each mash to determine the sterility of the fermentation.

Experimental Results

Effect of Amount of Inoculum

The amount of inoculum added ranged from 0 001% to 10% of the mash volume. To obtain the desired concentration of organisms in the inocula, dilutions were made from the original into sterile inoculum medium and 100 ml. was added to 1 litre of the 15% whole wheat mash.

In the first experiment the inoculum contained about 500 million organisms per ml. In the second experiment in order to obtain higher numbers, the inoculum was grown under reduced pressure for 24 hr., then concentrated to half the original volume by centrifuging and discarding the supernatant. This concentrated inoculum contained about 4000 million organisms per ml.

The results (Figs. 1A and 1B) show that the number of organisms added to the fermentation mash greatly influence the growth curve. High initial numbers induced shorter lag periods, shorter logarithmic growth and death periods, and greater numbers of organisms in the medium. These effects due to inoculum numbers were not quantitatively reproducible as a comparison of the growth curves for the two experiments show. The first three dilutions (10%, 1%, 0.1%) as shown in Fig. 1A contained the same numbers of bacteria as the last three dilutions (1%, 0.1%, 0.01%) shown in Fig. 1B. The relative effect found in each experiment is similar but the actual growth rates and numbers per ml. varied widely. This difference has been found in other experiments and appeared to be uncontrollable. Probably this variable culture activity was the main reason why rate experiments with this organism gave such irregular results.

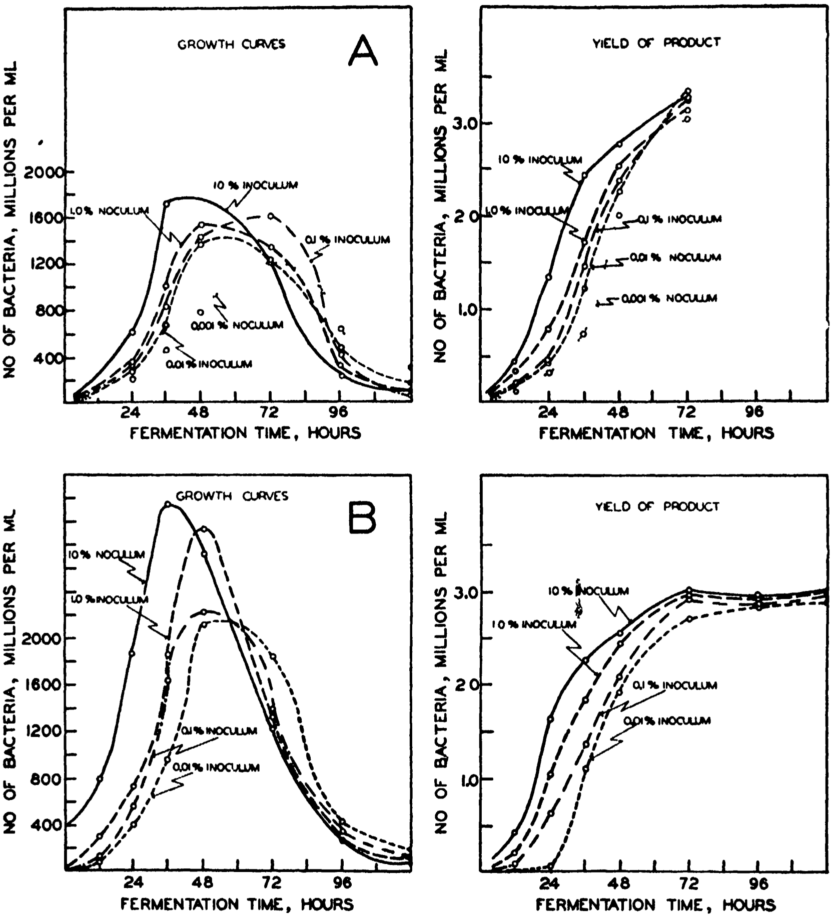

FIG. 1. *The effect of various amounts of inoculum on the growth of the culture and on the 2,3-butanediol yield on a 15% whole wheat mash A. The inoculum contained 500 million organisms per ml B. The inoculum contained 4000 million organisms per ml*

Marked variations in growth rate did not materially affect the product yield at 72 hr. As the growth rate increased the rate of 2,3-butanediol production also increased. Although the rate of carbohydrate dissimilation was shown to be dependent on the growth rate the amount of 2,3-butanediol produced in all of the samples was similar at 72 hr. However, this was to be expected because if all the carbohydrate is utilized a definite amount of 2,3-butanediol will be produced. A comparison of the growth curves and 2,3-butanediol production in both experiments showed that there was considerable 2,3-butanediol production after the maximum numbers of organisms had been reached. The numbers were still high at 72 hr., but in the second experiment little further 2,3-butanediol was produced, probably because most of the carbohydrate was utilized; however, where 0 01% inoculum was added there was a further increase at 96 hr.

These experiments showed that although the rate of growth and the rate of product formation were closely allied with the amount of inoculum added the yield of product at 72 hr. was not materially affected. Nor was the 2,3-butanediol yield at 72 hr affected by inherent differences in the ability of the culture to reproduce.

Effect of Nutrient Supplements

The addition of nutrient supplements to inoculum media is known to be advantageous to the growth of this organism when either whole wheat or starch is used as the substrate. The effect of various supplements at specified levels was measured by obtaining population trends in the inocula and by the effect of these inocula on the yield of products in a whole wheat fermentation. As a result of preliminary experiments and a consideration of the value in starch fermentation of various nutrients (4) six nutrient sources were compared: yeast extract (Difco), dried yeast, malt sprouts, Cerogras (dehydrated young oats obtained from the Greenmelk Co , Wallaceburg, Ont.), shorts, and corn steep liquor. Yeast extract was supplied at three levels (0.5%, 1.0%, 1.5%) and all other nutrients were added at the two lower levels.

Table I shows the effect on the population numbers of adding these nutrients to whole wheat inoculation medium. All these nutrients increased the numbers of organisms, with yeast extract showing the greatest effect. On the average, the 1.0% level of nutrient had little more effect than the 0 5% level. Where 1.0% and 1.5% yeast extract was added the growth peak had been passed by 36 hr.

The effect on the population numbers of adding these nutrients to starch inoculation medium is shown in Table II. Here, again, the addition of nutrients increased the number of organisms, with yeast extract giving the greatest effect. However, as starch is deficient in growth supplements the numbers in the control are much lower than found previously with whole wheat medium. The addition of nutrients had only a limited beneficial value.

TABLE I

EFFECT OF ADDED NUTRIENTS AT VARIOUS LEVELS ON THE GROWTH OF *Aerobacillus polymyxa* IN A WHOLE WHEAT INOCULATION MEDIUM

Nutrient	Amount added, %	Number of bacteria (direct count) in millions per ml.		
		12 Hr.	24 Hr.	36 Hr.
Control	0	500	630	1160
Yeast extract	0.5	670	1420	1690
	1.0	850	1780	1300
	1.5	720	1420	1120
Dried yeast	0.5	500	1020	1390
	1.0	580	1180	1240
Malt sprouts	0.5	450	1190	1380
	1.0	500	1290	—
Cerogras	0.5	620	1070	1540
	1.0	660	1330	1750
Shorts	0.5	510	940	1030
	1.0	510	760	—
Corn steep liquor	0.5	570	1010	580
	1.0	430	1010	1280

TABLE II

EFFECT OF ADDED NUTRIENTS AT VARIOUS LEVELS ON THE GROWTH OF *Aerobacillus polymyxa* IN A STARCH INOCULATION MEDIUM

Nutrient	Amount added, %	Number of bacteria (direct count) in millions per ml.		
		12 Hr.	24 Hr.	36 Hr.
Control	0	170	300	250
Yeast extract	0.5	460	600	700
	1.0	490	820	900
	1.5	450	670	1040
Dried yeast	0.5	220	430	710
	1.0	220	460	470
Malt sprouts	0.5	200	210	300
	1.0	200	320	340
Cerogras	0.5	230	310	460
	1.0	240	430	830
Shorts	0.5	380	480	480
	1.0	170	410	400
Corn steep liquor	0.5	300	400	340
	1.0	180	480	470

All of the above inocula with both whole wheat and starch as a substrate were used to inoculate 15% whole wheat mash at two inoculum levels. A statistical analysis of the yields of 2,3-butanediol obtained at 48 and 72 hr. showed that there were no significant variations due to the added nutrients. In Table III the results for the controls and yeast extract only are given. The yield of 2,3-butanediol at 48 hr. decreased in the controls as the inoculum with smaller numbers was added. The addition of yeast extract showed an effect at 48 hr. using starch inoculum but not using the whole wheat inoculum. There were no differences in the yields obtained at 72 hr.

TABLE III

EFFECT OF ADDING YEAST EXTRACT AT THREE LEVELS TO WHOLE WHEAT AND STARCH INOCULUM MEDIA ON THE 2,3-BUTANEDIOL YIELD AT 48 AND 72 HR.

Inoculum medium	Yeast extract added, %	Yield of 2,3-butanediol, %			
		3.0% Inoculum		0.1% Inoculum	
		48 Hr.	72 Hr.	48 Hr.	72 Hr.
Whole wheat	0.0	1.85	2.37	1.72	2.32
	0.5	1.47	2.31	1.91	2.42
	1.0	1.78	2.35	1.46	2.46
	1.5	1.50	2.22	1.88	2.36
Starch	0.0	1.62	2.26	1.42	2.43
	0.5	1.71	2.13	1.57	2.42
	1.0	1.84	2.40	1.61	2.54
	1.5	1.75	2.31	1.70	2.41

Effect of Inoculum Temperature

The optimum fermentation temperature in the range 30° C. to 37.5° C. has been previously reported (9) at 32.5° C. although differences were small and different strains gave varied results. In the present study a wider range of inoculum temperature was chosen (25° C., 30° C., 35° C., 40° C.) to demonstrate more clearly the effect on bacterial growth. Whole wheat inoculum was used both with and without 0.5% yeast extract. Numbers were estimated by the plate count method and are reported in Table IV.

The addition of yeast extract, as previously noted, greatly increased the bacterial numbers except at the highest temperature. After a microscopic examination the lower numbers at the higher temperatures were explained as it was found that as the temperature increased the length of the rods increased. This cessation of cell division while cell elongation continues normally has been reported elsewhere on numerous occasions and was observed to occur spontaneously or as a result of the presence of drugs or other foreign substances (5). This phenomenon was also noted at the end of a very rapid fermentation by *Aerobacillus polymyxa.*

TABLE IV

EFFECT OF TEMPERATURE AND ADDED YEAST EXTRACT ON THE GROWTH OF *Aerobacillus polymyxa* IN A WHOLE WHEAT INOCULATION MEDIUM

Temperature, ° C	Number of bacteria (plate count) in millions per ml.			
	No nutrient added		0.5% Yeast extract added	
	12 Hr	24 Hr.	12 Hr	24 Hr.
25	0.9	4	7.1	44
30	0.2	27	3.5	83
35	0.4	9	0.4	22
40	0.1	17	0.6	8

When the inocula were used to ferment a whole wheat mash there was no significant variation in the 2,3-butanediol yield due to temperature or nutrient at either the 3.0% or 0.1% inoculum level at 48 or 72 hr. The results using 3.0% inoculum are given in Fig. 2.

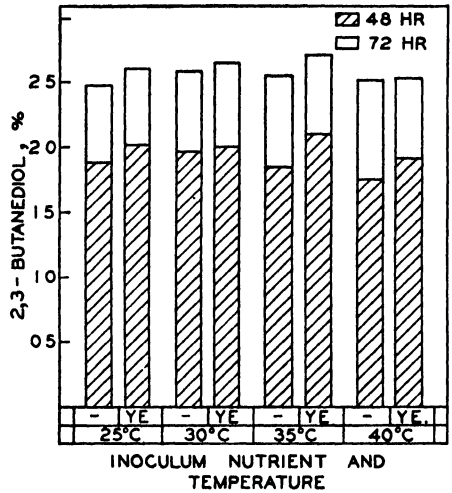

FIG. 2. *The effect of the incubation temperature used on whole wheat inoculum, with and without added nutrient, on the 2,3-butanediol production in a 15% whole wheat mash using 3.0% of inoculum.*

Effect of Aeration and Reduced Pressure

Preliminary experiments indicated that inoculum numbers were increased greatly by aeration or reduced pressure. Table V gives the number of organisms found in whole wheat medium after aeration or reduced pressure for 24 hr. The effect of adding yeast extract was found for each treatment. For the most part, the numbers in the inocula under reduced pressure and aeration were very similar and were approximately double the controls. Yeast extract always increased the numbers. Apparently the higher levels of aeration and reduced pressure had no further effect but it was suspected that owing to the greatly increased growth rate the period of optimum numbers had been passed at 24 hr.

TABLE V

EFFECT OF AERATION, REDUCED PRESSURE, AND ADDED YEAST EXTRACT ON THE GROWTH OF *Aerobacillus polymyxa* IN A WHOLE WHEAT INOCULATION MEDIUM

Treatment	Number of bacteria (direct count) in millions per ml. at 24 hr.	
	No nutrient added	0 5% Yeast extract added
None	600	1100
Aeration (100 ml./litre/min.)	1150	2600
Aeration (500 ml./litre/min.)	1200	1950
Pressure (20 in. Hg absolute)	1300	1900
Pressure (10 in. Hg absolute)	310	2180

As it was thought that these inocula might have an effect on the ratio of products formed, ethanol and 2,3-butanediol were determined at 72 hr. The results are given in Table VI for the two inoculum levels. At 48 hr. the 0.1% level of inoculum gave lower yields than did the 3 0% level. Aeration of the inoculum gave an increased yield at 48 hr. of 2,3-butanediol at the 3.0% inoculum level but showed little benefit at the lower level of inoculum. When the inoculum numbers under reduced pressure are considered, the yields of 2,3-butanediol were inconsistent at 48 hr., again suggesting that the culture was not in the logarithmic growth phase when used. After 72 hr. fermentation the yields of 2,3-butanediol were practically constant using 3.0% inoculum but were less constant using the 0.1% level and, here, the addition of yeast extract had some effect. The ethanol yields varied little. The effect of aeration or reduced pressure on the inoculum was marked but there was no change in the yield of products in the subsequent fermentation.

A fermentation was carried out under reduced pressure to investigate further the effect on bacterial numbers. Thirty millilitres of inoculum was used to inoculate 1 litre of whole wheat mash in 4-litre bottles. A pressure of 15 in. of mercury was maintained in one flask. The growth curves given in Fig. 3 and the yields of 2,3-butanediol for the first 48 hr. given in Table VII are an average of two experiments.

Bacterial numbers in the control followed the normal type of growth curve but reduced pressure had a great effect on all phases of the curve. The lag period was shorter, the growth rate was more rapid, the period of maximum numbers was short and the death rate was high. Reduced pressure also increased the fermentation rate as the 2,3-butanediol yields show. However,

TABLE VI

EFFECT OF INOCULUM TREATMENT (AERATION, REDUCED PRESSURE, ADDED NUTRIENT) ON THE PRODUCT YIELD IN 15% WHOLE WHEAT MASH

Treatment	Yeast extract, %	48 Hr.	72 Hr.		
		2,3-Butanediol, %	2,3-Butanediol, %	Ethanol, %	Ratio, diol/ethanol
A. 3.0% Level of inoculum					
None	None 0.5	1.66 1.72	2.57 2.58	1.58 1.49	1.63 1.73
Aeration (100 ml./litre/min.)	None 0.5	1.88 1.92	2.49 2.58	1.50 1.53	1.66 1.68
Aeration (500 ml./litre/min.)	None 0.5	2.13 2.21	2.52 2.53	1.54 1.65	1.64 1.53
Pressure (20 in. Hg absolute)	None 0.5	1.95 1.73	2.41 2.36	1.51 1.50	1.60 1.57
Pressure (10 in. Hg absolute)	None 0.5	1.69 1.70	2.48 2.48	1.52 1.53	1.63 1.63
B. 0.1% Level of inoculum					
None	None 0.5	1.48 1.56	2.28 2.52	1.30 1.52	1.75 1.66
Aeration (100 ml./litre/min.)	None 0.5	1.42 1.91	2.43 2.51	1.36 1.56	1.79 1.61
Aeration (500 ml./litre/min.)	None 0.5	1.64 1.63	2.38 2.44	1.40 1.40	1.70 1.74
Pressure (20 in. Hg absolute)	None 0.5	1.54 1.55	2.34 2.40	1.29 1.42	1.81 1.69
Pressure (10 in. Hg absolute)	None 0.5	1.37 1.59	2.30 2.61	1.25 1.43	1.84 1.82

Adams and Leslie (2) have shown that the final yield of 2,3-butanediol under reduced pressure was lower than normal owing to the induced anaerobic conditions and resulted in a higher ethanol yield with a low 2,3-butanediol to ethanol ratio. The effect of reduced pressure was to increase greatly the actual bacterial population and thus to increase the fermentation rate.

Effect of 'Backstocking'

This method of inoculation has long been standard brewing technique and has been found useful in other fermentations. Preliminary experiments showed that growth was at a maximum between 36 and 48 hr. in the fermentation of 15% whole wheat mash under normal conditions; thus samples taken at 36 hr. were used for inoculum. This ensured that the bacterial culture was still in the logarithmic growth phase.

Inoculum was first prepared in a normal manner and the 3.0% level was used to inoculate the first flasks. The experiment was run in duplicate and the results averaged. After 36 hr., inoculum was obtained from these mashes

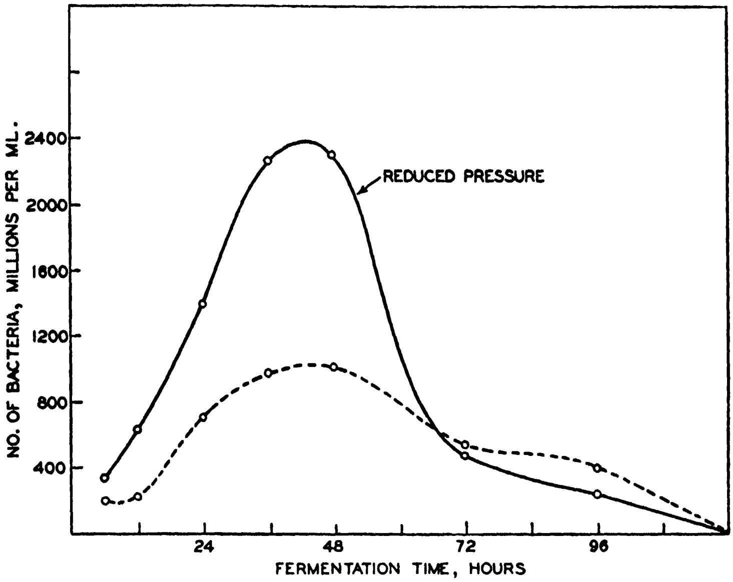

Fig. 3. *The effect of reduced pressure on the bacterial numbers in a 15% whole wheat fermentation mash.*

TABLE VII

Effect of reduced pressure on the yield of 2,3-butanediol (%) in a 15% whole wheat fermentation mash

	Time in hours				
	6	12	24	36	48
Control	0.41	0.47	0.84	1.13	1.88
Pressure (15 in. Hg absolute)	0.33	0.56	1.22	1.82	2.42

and used to inoculate the second set of flasks. This operation was repeated five successive times. Direct counts and 2,3-butanediol yields were estimated at 36 hr. and 2,3-butanediol content and pH at 72 hr. Aseptic technique was used and there was no evidence of contamination. The results are given in Fig. 4.

Although the inoculum was first grown in inoculum medium this had no effect on the bacterial numbers of the first transfer as compared to those succeeding. There was no increase or decrease in the numbers, pH, or 2,3-butanediol yields through the successive 'backstocking' operations.

Discussion

It is evident that any treatment that produces an increase or decrease in inoculum numbers can be equalled by using more or less of the untreated inoculum, if the treatment has produced no change in the fermentative ability of the bacteria. In all of the fermentation results the yield of 2,3-butanediol at 72 hr. remains unchanged and the effect of a treatment that increased inoculum numbers is only to increase the initial fermentation rate with no effect on the ratio of products formed.

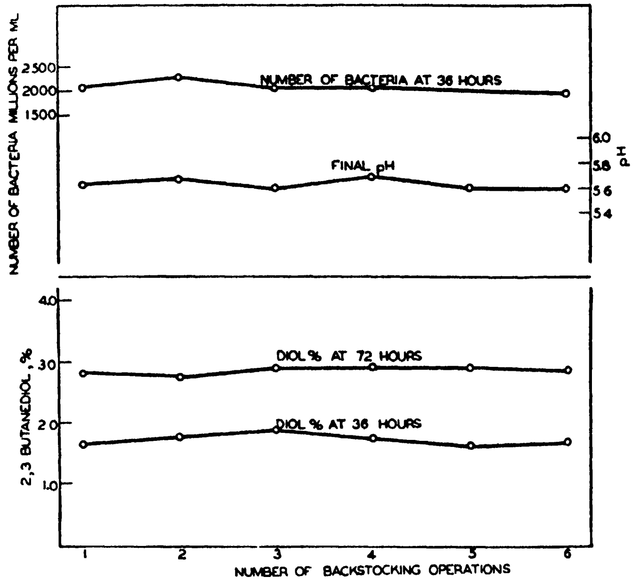

FIG. 4 *The effects of a number of successive 'backstocking' operations on bacterial numbers, final pH, and 2,3-butanediol production.*

In large scale operations the fact that a good yield of 2,3-butanediol is obtained with a small amount of inoculum is very important. Added nutrients are unnecessary, incubation temperature is not critical, and reduced pressure and aeration of the inoculum, while increasing the growth rate, do not affect the product yield; these facts are also of practical importance. Providing aseptic techniques can be applied, 'backstocking' should prove to be a useful and economical operation in this fermentation.

The growth phases of bacteria have been studied for a considerable time and Rahn (10), Buchanan and Fulmer (3), Winslow and Walker (11), Hinshelwood (5), and others have reviewed the literature. The interrelation of the causes of growth and death are not clearly understood. The addition of larger numbers of bacteria to the fermenting medium is known to decrease the 'lag' phase and our results show this (Fig. 1). Rahn (10, p. 402) has shown that the effect of a small inoculum was only to lengthen the time taken to reach the maximum numbers obtained with a large inoculum. This was found in our results but, in addition, there was a marked increase in the maximum numbers attained as greater initial numbers were added. It is difficult to suggest a logical reason for this phenomenon.

The rate of autolysis is inversely related to the growth rate and is thus faster where the larger amounts of inoculum are used. At maximum numbers the amount of 2,3-butanediol formed is always about 2% but it is not clear whether the rapid death rate is due to accumulation of toxic products, exhaustion of the substrate, or an interaction of these factors. It is improbable that a lack of nutrient and carbohydrate sources can alone explain the effects found although Jordan and Jacobs (6) have shown in their controlled experiments that bacterial numbers varied directly as the food supply.

There is a considerable production of 2,3-butanediol in the 'death' phase. The slower fermentation rate in this phase is found where the larger inoculum is used and thus the benefits of using a large inoculum are nullified. If it were possible to obtain maximum product yields at the same time as maximum numbers are found, the benefit of the larger inoculum would be considerable. A better understanding of the factors affecting bacterial growth might allow this condition to be attained.

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THE FRICTION OF HEATED SLEIGH RUNNERS ON ICE[1]

By P. M. Pfalzner[2]

Abstract

An attempt was made to reduce the sliding friction of sleigh runners on ice at 20° F., 0° F., and −10° F. by applying heat to the runners. The efficiency of this method was found to be less than 20%. Some doubt is thrown on the simple theory that the low friction on ice is due to a lubricating film of water.

Introduction

It is common experience that the friction of ice increases at low temperatures (1; 4, p. 393) and at −140° C. it is of the same order as that found for other unlubricated solids. Sleighs play an important part in transportation in Canada, and it was felt that an attempt should be made to investigate means of lowering the sliding friction on snow and ice surfaces. Two theories have been advanced to account for the ease of sliding on snow and ice at ordinary temperatures, the theory of pressure melting, and the theory of melting due to frictional heating. Klein (2) who has worked with light loadings per sq. in. has favoured the melting-by-friction theory while Wakefield (5) working with higher loadings holds that there is a definite change in the friction after a particular loading is reached under given conditions (3). Again Bowden and Hughes (1) are inclined to support the melting-by-friction theory.

Common to both these theories, however, is the surmise, that some surface melting of the snow or ice occurs, and the resulting thin film of water acts as a lubricant. It would thus appear that, if heat were supplied to sleigh runners, the process of melting at low temperatures would be facilitated, and, it was hoped, that the friction would be substantially reduced thereby. It was decided to make experiments on ice surfaces rather than on snow, since ice is easier to make and is of a more uniform nature than snow.

Description of Apparatus

The experiments were carried out on a turntable driven by an electric motor, the speed being variable by means of a rheostat. On this table a circular track was built into which water was poured and allowed to freeze. The outside radius of the track was 19 in., inside radius 13 in. The surface of the ice was smoothed by a cylindrical heating element that could be lowered to the track; the axis of the cylinder was horizontal and at right angles to the direction of motion of the surface. It was found that the water formed by the melting of the ice had to be dried off, otherwise it was inclined to freeze again and the surface was not properly finished. The drying of the ice could conveniently be done with a cotton cloth soaking up the water on the turntable just beyond the heated cylinder. Small model sleighs were used, about 3½ in. long, 2¾ in. wide, having two nichrome runners, ⅛ in. wide through which electric current could be passed. The sleigh was attached to a fixed point by a calibrated spring, thus being held stationary on the moving ice track, while the extension of the spring gave a measure of the friction between the ice and sleigh runners.

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Contribution from the Heat Section, Division of Physics and Electrical Engineering, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1510.

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Experimental Method

A known load was placed on the sleigh, and the turntable set in motion at a rate of about 40 to 60 r.p m The extension of the spring holding the sleigh was read, first without passing any current through the runners, then with currents from 2 to 10 amp passing. The power input was known, and the power usefully expended in lowering the friction was calculated from the reduction in the frictional force due to the heating current and from the speed of revolution.

It was found that rather less than 10% of the power input was useful; it was then decided to pass the current through the front part of the runners only rather than through their whole length; this resulted in some saving of power input but did not raise the efficiency appreciably.

Results and Discussion

The actual figures obtained during the tests are given below in Table I. The following is an outline of the calculations. the radius of the turntable, measured from the centre to halfway between the runners, was 16 in The saving in work was therefore $2\pi \times 16/12 \times N \times F$ ft. lb /min , where N is the number of revolutions per minute, and F is the difference in force as measured by the spring when the runners are unheated and when they are heated The expenditure of electrical energy to get this saving was given by the power supplied in watts, and hence, using the relation 1 ft. lb./min. = 0.0226 w., the efficiency is readily obtained. The important thing to note in Table I is that the electrical energy expended simply disappears for the most part, and no matter how much power is put in, the efficiency at 20° F. is only about 10%, and at most 18% at −10° F. Furthermore the advantage in heating merely the front of the runners instead of the whole is relatively small.

The results were rather unsatisfactory in so far as the existing theory was concerned, because, if the crucial factor in low friction is a film of water, experience in other connections shows that direct heating is more economical than frictional heating. It was decided to take the temperature of the runners by a thermocouple placed in contact with the runners. In Table II temperatures are given with the sleigh on and off the ice at 20° F.

These results show that the runners attain the temperature of melting ice immediately when placed in contact with the ice surface. Although the runners were heated by currents as large as 10 amp., and temperatures of

TABLE I

THE EFFICIENCY OF ELECTRICALLY HEATED RUNNERS

Conditions of experiment	Speed of turntable r p m	Spring tension			Power saved, w	Heating current		Power supplied, w.	Efficiency, %
		Runners unheated oz	Runners heated, oz	Difference oz		Amp	Volts		
Whole length of runner heated	45	7 50	6 25	1 25	0 67	6 6	1 1	7 2	9
Temp 10° F load 11 lb approx	49	9 00	8 00	1 00	0 57	6 6	1 1	7 2	8
Front of runner only	34	8 00	7 50	0 50	0 20	6 9	0 2	1 4	14
heated	39	6 25	5 75	0 50	0 24	9 0	0 25	2 25	10
Temp 10° F, load 11 lb approx	36	7 25	6 50	0 75	0 32	9 0	0 2	1 8	18
Front of runner only	39	3 0	2 0	1 0	0 46	9 0	1 3	11 7	4
heated	39	3 0	2 25	0 75	0 35	6 0	0 8	4 8	7
Temp 20° F, load	41	3 0	2 5	0 5	0 23	3 0	0 4	1 2	2
11 lb	41	3 0	3 0	0	0	2 0	0 3	0 6	0
Front of runner only	53	4 25	4 25	0	0	2 0	0 3	0 6	0
heated	53	4 25	4 00	0 25	0 16	4 0	0 6	2 4	7
Temp 20° F load	53	4 25	3 30	0 95	0 52	6 0	0 9	5 4	10
15 lb	53	4 25	2 75	1 50	0 94	8 0	1 2	9 6	10
	53	4 00	2 65	1 35	0 89	10 0	1 5	15 0	7
Front of runner only	45	4 5	3 5	1 0	0 53	10 0	0 6	6 0	9
heated	60	4 7	3 7	1 0	0 71	10 0	0 6	6 0	12
Temp −10° F load	60	4 8	4 0	0 8	0 57	8 0	0 4	3 2	18
4 lb	60	4 8	4 3	0 5	0 36	6 0	0 35	2 1	17

TABLE II

THE TEMPERATURE OF THE HEATED RUNNERS (ICE AT 20° F.)

Heating current		Sleigh off the ice		Sleigh on the ice, moving	
Amp.	Volts	Potentiometer milliamp.	Temp., ° F.	Potentiometer milliamp.	Temp., ° F.
6	0 4	1 36	94	0	32
8	0 6	2 56	144	0	32
10	0 7	4 19	209	0	32
0	0	−0 194	22	−0 140	25

over 200° F. were recorded off the ice, the friction fell very little. It is of interest to note, however, in Table I, that the benefit derived by heating the runners is considerably greater at −10° F. than at +20° F. Hence if this heat can be obtained very cheaply, say by special charcoal burners built into steel runners or by heat from the exhaust of the tractor, an improvement of perhaps 20% might be realized in very cold weather.

Acknowledgments

The author wishes to acknowledge with gratitude the interest shown by Dr. C. D. Niven throughout the course of these experiments, and the most valuable assistance rendered by Mr. S. J. Brunette in building the turntable, assembling the equipment, and working out a method for smoothing the ice surface.

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DRILL FOR DETERMINING THICKNESS OF ICE[1]

By T. D. Northwood[2]

Abstract

A device is described for quickly drilling through ice to determine its thickness. It consists of an electric heater mounted at the tip of a rod long enough to penetrate to the desired depth. The unit drills a half inch diameter hole at the rate of about two feet per minute. It operates from a 6 v. storage battery and requires about the same power as an automobile starting motor.

It was recently required to develop a quick method of measuring the thickness of ice formed on lakes or rivers to determine the maximum load it would bear. The method that seemed most practical was to drill a hole through the ice, noting the depth of the drill up to the moment when it plunged through the ice. Some mechanical drills were tried and found to be moderately successful at temperatures near the freezing point. However, these failed at subzero temperatures, where ice becomes glass-like in hardness. More successful was a heater device that melts a half inch diameter hole in the ice. This was very satisfactory, being capable of drilling through about two feet of ice in one minute.

The construction of the final model is illustrated in Fig. 1. It consists essentially of a rod long enough to penetrate the desired range of thickness, with an electrically heated tip. A 6 v. storage battery was chosen as a convenient, portable source of power. This necessitated a heating element with a resistance of about 0.05 ohms, to dissipate the necessary power. The other components of the electrical circuit have a lower order of resistance, although the brass tubing that forms the outer conductor becomes warm enough to ensure that it does not freeze in.

The heating element is a piece of projector carbon (National No. 587) shaped to fit between the outer tubing and a retaining screw, which is tapped into the central brass rod. Since the carbon becomes red hot, even when immersed in ice water, it must be carefully designed to ensure reasonably long life. A large contact area is provided at each end of the element to avoid overheating at these points and consequent deterioration of both brass and carbon. Otherwise a fairly uniform distribution of heat was found desirable to avoid uneven expansion and cracking.

The retaining screw is held firmly against the bottom of the carbon by a spring at the upper end of the central rod. This maintains a good electrical contact in spite of thermal expansion effects and possible crumbling of the contact surfaces of the electrode. The spring tension may be released by pressing a knob on the handle. This facilitates the removal of the

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[2] *Physicist.*

retaining screw and replacement of the carbon if necessary. In limited trials of the final design in the laboratory the carbon appeared capable of lasting indefinitely. However, it is rather fragile and might be broken by rough handling.

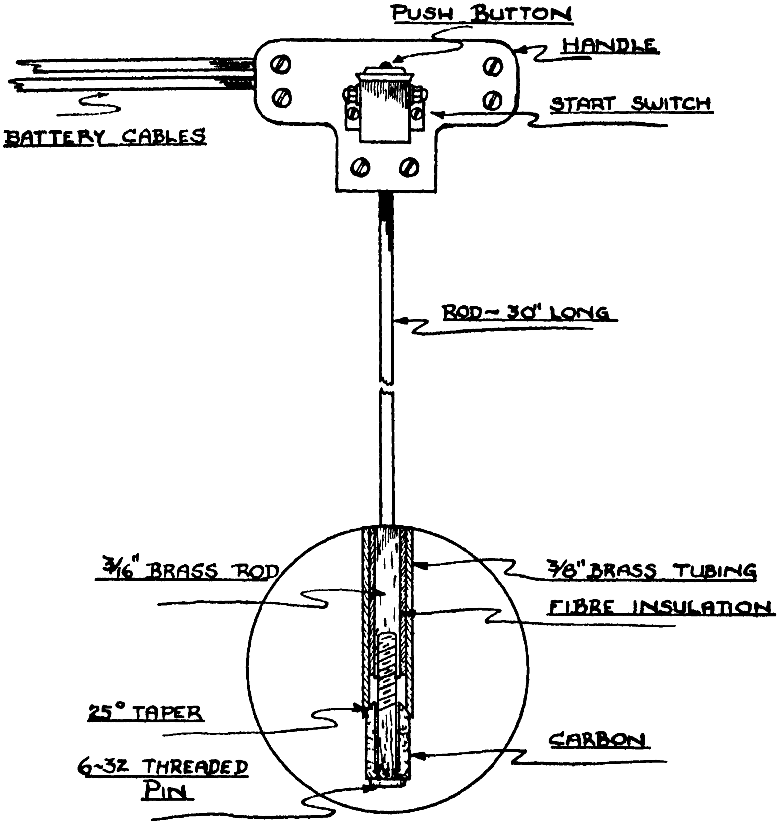

FIG 1 *Drawing showing essential features of ice drill*

Since the electrical load is about equal to that involved in starting an automobile, a standard automobile starting relay was used for switching This is mounted on the handle in such a way that it may be operated as a push-button. Short flexible cables make connection to a carrying-case containing the storage battery. It is, of course, necessary to re-charge the battery after about a dozen operations.

THE SOLVENT EXTRACTION OF CRUDE MUSTARD GAS[1]

By R. Mungen[2] and H. Sheffer[3]

Abstract

Equilibrium studies with low-boiling hydrocarbon fractions and crude mustard gas indicate that the latter can be extracted to give product purities of approximately 92 5% with 95% recovery. These values have been verified in the operation of a pilot plant for continuous counter-current extraction of crude mustard gas.

One of the simplest and least expensive processes for the manufacture of mustard gas involves the direct reaction of ethylene with sulphur monochloride. A product containing approximately 70% β,β'-dichlorodiethyl sulphide is obtained. Because of the cheapness of the product it is justifiable to purify it by means of an additional process, if material richer in β,β'-dichlorodiethyl sulphide is desired. As part of a general program to attempt to purify the crude material, a solvent extraction process was extensively investigated in these Laboratories.

In 1920 Thompson and Odeen (2) reported an investigation made at Edgewood Arsenal, indicating that some hydrocarbons can be used in the solvent extraction of crude mustard gas to effect a purification. A detailed investigation of equilibrium data and application to pilot plant is described here.

Nature of Crude Mustard Gas

The samples of crude mustard gas used in this investigation were dark brown in colour, contained approximately 70% by weight of β,β'-dichlorodiethyl sulphide, and had melting points ranging from 5 9° to 6.5° C. The impurities present are complex in nature and have not been completely determined. Organic polysulphides as well as free sulphur in a colloidal form are known to be present. Sulphur is readily precipitated on addition of many types of chemicals (e.g. ammonia) to the crude material. During distillation a black tarry residue is formed. In any purification process it would be desirable to avoid decomposition due to excess heating or chemical reaction.

Solubility Studies of Solvents for β,β'-Dichlorodiethyl Sulphide

Studies of the solubility of crude mustard gas in a large number of organic solvents were undertaken to find a suitable solvent for the extraction of β,β'-dichlorodiethyl sulphide. The majority of these liquids were completely miscible with the crude material at ordinary temperatures. Others reacted with it, in many cases precipitating sulphur. It was concluded that hydrocarbons in the pentane boiling range were the most suitable solvents for the purification of crude mustard gas.

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Contribution from Chemical Warfare Laboratories, Ottawa.

[2] *Formerly Major, Canadian Army; present address, Massachusetts Institute of Technology, Cambridge, Mass.*

[3] *Major, Canadian Army.*

Extraction Experiments

Single Batch Extractions

Initial extraction experiments were carried out by shaking crude mustard gas with solvent in a separatory funnel. After separation, the solvent layer was removed and analysed.

Crude material, containing 70% by weight of β,β'-dichlorodiethyl sulphide, was extracted with an equal volume of petroleum ether (boiling range 30° to 60° C.). When the solvent was removed from the resulting solvent layer, a product of approximately 80% purity was obtained. From this it is seen that a partial purification can be made using solvent extraction.

Continuous Extraction

A small glass column (1 in. inside diameter, 4 ft. long) was built to study continuous counter-current extraction of β,β'-dichlorodiethyl sulphide from the crude material. The specific gravity of the mustard gas was 1.3 and that of the solvent 0.65. The flow rate of the crude mustard gas feed was 10 ml. per minute and the solvent flow rate was varied to give solvent/feed ratios (by weight) of from 1/1 to 6/1.

It was found that about 85% of the available β,β'-dichlorodiethyl sulphide could be extracted as an 80% pure product using a solvent/feed ratio of 5/1. Using a solvent/feed ratio greater than this increased the yield but reduced the purity of the product.

From this result it was apparent that products of high percentage purity with good recovery could be obtained only from a complete extraction system including rectification. More complete equilibrium data were required to continue work on a pilot plant scale.

Equilibrium Studies

The solvent, chosen from a consideration of cost, availability, and solvent properties was 'Skellysolve *A*,' a mixture of pentanes with a boiling range of 93° to 97° F., 60% boiling at 94° F.

For the equilibrium studies the crude material is considered to be a two component system, β,β'-dichlorodiethyl sulphide (hereafter designated '*H*') and *I* (*I* = impurities). The data are based on the three component system 'Skellysolve *A*'-*H*-*I*.

In order to obtain a wide range of points on the equilibrium curve, it was necessary to have mustard gas samples of a wide range of purities. Samples rich in *H* were obtained by adding extracted material to nearly pure *H* or vice versa. Samples low in *H* and high in *I* content were obtained by continued re-extraction of the crude mustard.

All the batch extractions were carried out at 25° ± 0.01° C. in three-necked flasks, fitted with stirrers. Sufficient quantities of solvent and mustards of various purities were used to give at least 100 gm. of solvent-free extract and residue in each case. After being stirred for 30 min., the contents of the flasks were allowed to settle into two layers. These were carefully sampled after the attainment of equilibrium. The bulk of the solvent in each portion was removed by distillation, the last traces being removed under vacuum. From the weight loss the percentage of solvent was obtained.

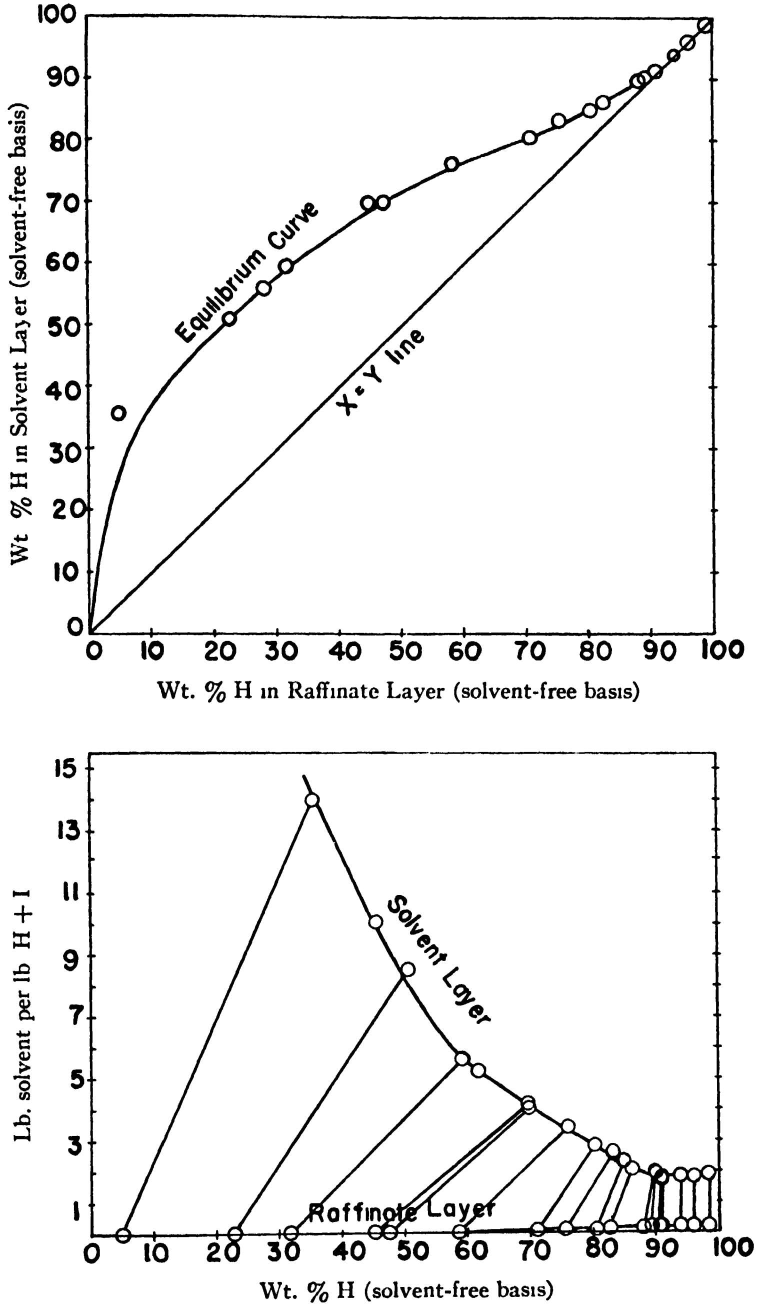
The *H* contents of the solvent-free extracts and raffinates were obtained by means of vacuum distillation using a standardized method. Corrections for impurities carried over during distillation were made on the basis of melting points of the distillates. Verification of the distillation data could be made by means of sulphur analyses, since a straight line relationship was found to exist between total sulphur content and purity of the mustard gas samples. For samples approaching 100% in *H* content, the distillation method gave results with a reproducibility of 0.2%. As the purities were lowered the results were less accurate. Care had to be taken in the distillation of raffinates low in *H* because of decomposition and evolution of gases on heating the material under vacuum. On such samples, therefore, the distillation results may be in considerable error. However, in the case of the raffinate with the lowest *H* content (5%), an error of as much as 100% would not affect the position of the equilibrium curve a great deal.

TABLE I

EQUILIBRIUM DATA—SYSTEM 'SKELLYSOLVE *A*'-*H*-*I* AT 25°C.

Composition of extract (solvent layer)				Composition of raffinate (extracted crude layer)			
% *H*	% *I*	% Solvent	% Purity (solvent-free)	% *H*	% *I*	% Solvent	% Purity (solvent-free)
34.0	0.3	65.7	99.1	81.2	0.7	18.1	99.1
33.7	1.3	65.0	96.2	78.8	3.0	18.2	96.3
32.9	2.1	65.0	94.0	76.5	4.9	18.6	94.0
32.8	3.2	64.0	91.2	74.2	7.3	18.5	91.0
31.9	3.1	65.0	91.1	73.6	7.5	18.9	90.7
30.4	3.3	66.3	90.1	74.0	8.9	17.1	89.3
30.0	3.3	66.7	89.9	72.4	9.6	18.0	88.3
27.9	4.4	67.7	86.3	69.3	14.5	16.2	82.7
25.4	4.5	70.1	85.0	68.9	16.6	14.5	80.6
23.0	4.6	72.4	83.3	66.3	21.4	12.3	75.6
21.0	5.1	73.9	80.4	63.1	25.6	11.3	71.1
17.2	5.4	77.4	76.2	53.5	37.9	8.6	58.6
13.9	6.0	80.1	69.9	44.6	49.3	6.1	47.6
13.4	5.8	80.8	69.8	42.1	51.3	6.6	45.1
9.9	6.1	84.0	61.9	—	—	—	—
8.9	6.1	85.0	59.4	30.3	64.7	5.0	31.9
7.2	5.7	87.1	55.8	27.1	69.3	3.6	28.1
5.4	5.2	89.4	50.9	22.0	74.3	3.7	22.9
4.1	4.9	91.0	45.7	—	—	2.9	—
2.4	4.3	93.3	35.5	4.9	92.6	2.5	5

The equilibrium data are given in Table I and are represented graphically in Figs. 1 and 1*a*.



FIGS. 1 and 1*a*. *Equilibrium data.*
System 'Skellysolve A'-H-I at 25° C

Pilot Plant Application of Equilibrium Studies

The method of treating the equilibrium data was that given by Maloney and Schubert (1). The equilibrium data were used to calculate the operational variables of the extraction column. These include solvent dosage, reflux ratio, and number of transfer units for a given separation. The results of these calculations based on enlargements of Figs. 1 and 1*a* are given in Table II. Figs. 2, 3, and 4 give the number of theoretical contact units for recoveries of 85, 90, and 95% at purities of 85, 90, and 92.5%.

TABLE II

T.C.U.'S AS A FUNCTION OF REFLUX RATIO FOR VARIOUS *H* RECOVERIES, *B*, AND PRODUCT PURITIES, X_E

Reflux ratio		X_E = 92.5%			X_E = 90%			X_E = 85%		
	B	85	90	95	85	90	95	85	90	95
	X_R	29.4%	21.9%	12.5%	31.2%	23.5%	13.5%	35.0%	27.1%	16.1%
4	$m + n$	27.4	27.8	28.5	9.4	9.7	10.4	4.3	4.9	5.3
	m	3.4	3.8	4.5	2.6	3.0	3.4	2.0	2.6	3.0
6	$m + n$	21.8	22.2	22.8	8.3	8.8	9.2	3.9	4.3	4.8
	m	2.8	3.2	3.8	2.3	2.8	3.2	1.9	2.3	2.8
8	$m + n$	19.5	19.9	20.3	7.6	8.2	8.6	3.8	4.2	4.6
	m	2.5	2.9	3.3	2.0	2.6	3.0	1.8	2.2	2.6
10	$m + n$	18.9	19.2	19.6	7.4	8.0	8.2	3.7	3.9	4.2
	m	2.3	2.6	3.0	1.9	2.5	2.7	1.7	1.9	2.2
20	$m + n$	17.6	17.9	18.3	6.9	7.5	7.7	3.5	3.7	3.9
	m	2.1	2.4	2.8	1.7	2.3	2.5	1.6	1.8	2.0
∞	$m + n$	16.9	17.2	17.5	6.0	6.8	7.0	3.3	3.5	3.7
	m	1.7	2.0	2.3	1.7	2.0	2.2	1.6	1.8	2.0

T.C.U = *theoretical contact unit*
m = *T.C.U's for stripping section*
n = *T.C.U's for enriching section.*
X_R = *H content of raffinate.*

From the equilibrium data it is apparent that it is not possible to obtain 100% pure β,β'-dichlorodiethyl sulphide from the crude material using a solvent extraction process with pentane fractions as the solvent. The maximum purity that can be expected with a reasonable number of contact units and practical reflux ratio is about 92.5%. From the small column extractions and the equilibrium data it was possible to estimate the height of a theoretical contact unit. This height was found to vary markedly with flow rates, but for practical flows was from 3 to 5 ft.

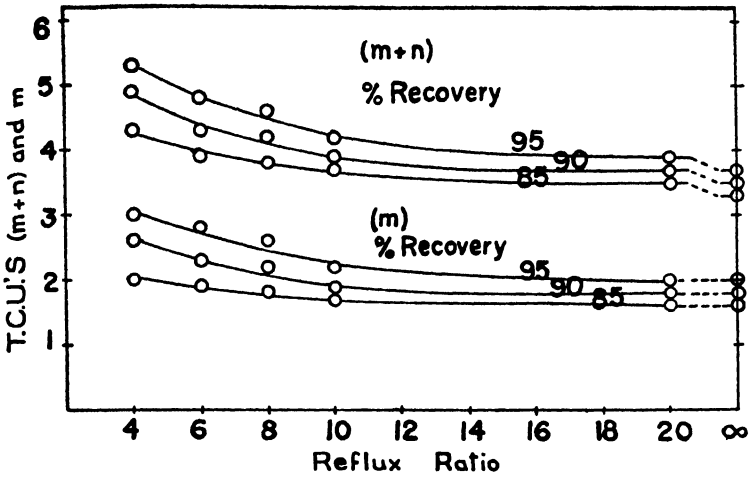


FIG. 2. *Theoretical contact units required to produce 85% product purity as a function of reflux ratio for various H recoveries.*

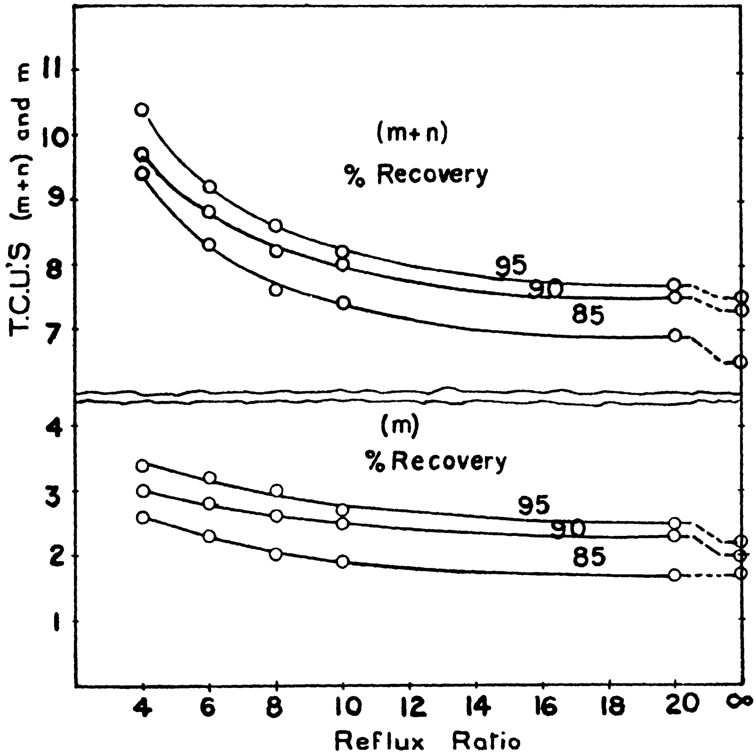


FIG. 3. *Theoretical contact units required to produce 90% product purity as a function of reflux ratio for various H recoveries.*

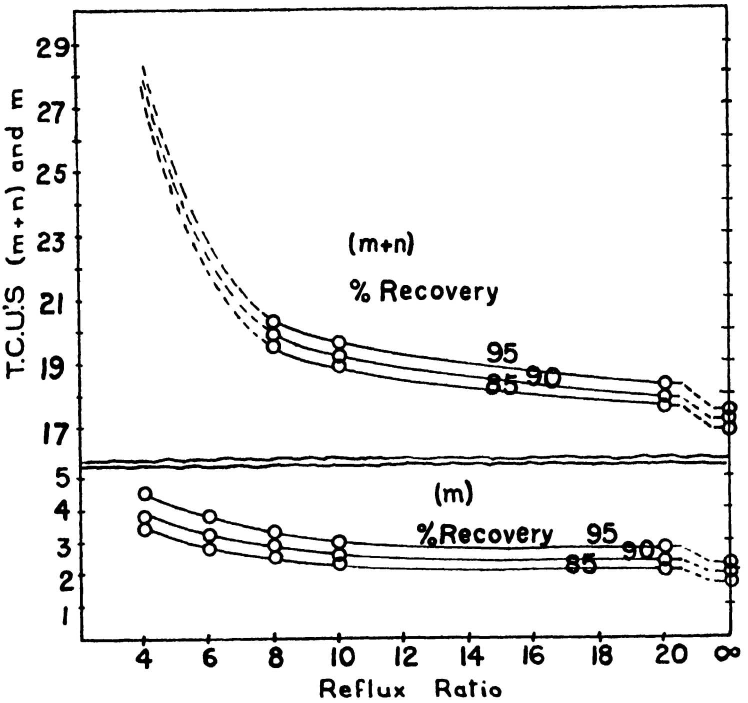


FIG. 4. *Theoretical contact units required to produce 92.5% product purity as a function of reflux ratio for various H recoveries.*

The Pilot Plant

The arrangement of the pilot plant equipment is shown schematically in Fig. 5. The unit was built to accommodate a feed capacity of about 500 lb. per day. The plant was installed in an old ventilation shaft that was of such a height as to allow the installation of about 38 ft. of useful column length.

The extraction column was of standard 4-in. iron pipe assembled from 6-ft. lengths with standard couplings. The packing was ½-in. glass raschig rings. The column was wound with resistance wire over its entire length and insulated with 'rock-wool' to permit temperature regulation. The crude feed entered at the 12 ft. level.

The solvent stripper was made of 14 gauge, 18-8 stainless steel 10 ft. long and 2 in. in diameter. It was fitted with a steam jacket operated at 5 to 10 lb. steam pressure.

The product cooler was a water-jacketed 18-8 stainless steel tube ⅜-in. I.P.S., 6 ft. in length. The solvent condenser was of the ordinary tube variety made of mild steel. The condenser was 5 ft. long, 6 in. in diameter, and had 17 ¼-in. I.P.S. tubes. The cooling water flowed through the tubes.

The feed pump was a Hills-McCanna proportionating pump. The solvent reflux pumps were rotary gear pumps made by the Viking Pump Co.

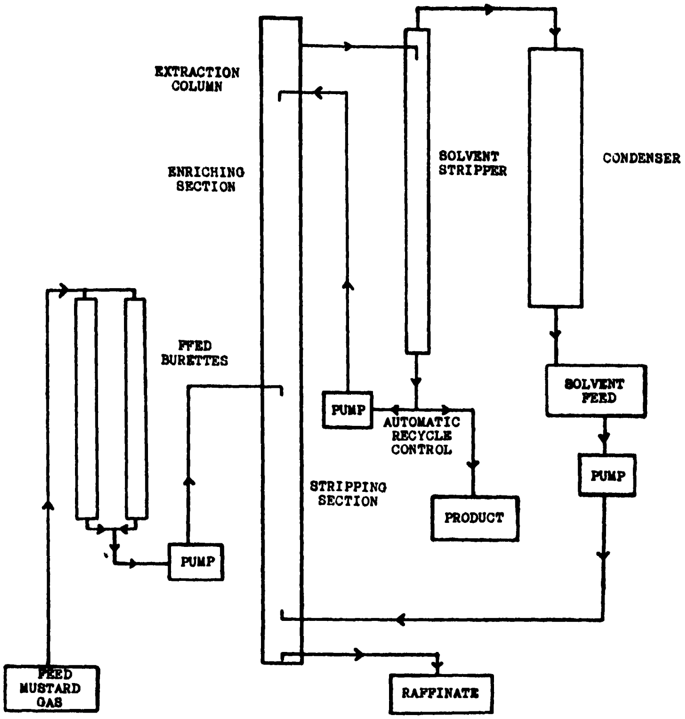


FIG 5 *Flow diagram, pilot plant.*

The recycle regulator was operated magnetically on a time ratio Since this is common practice it is not described in detail.

The feed burettes were made of 3-in. I P.S. mild steel, 4 ft. long, fitted with full length sight-gauges. They were calibrated in 100 ml. units and served to adjust the feed rate of the pump. The two burettes were arranged so that one could be filled while the other supplied the pump with feed liquid. The line from the feed drum to the burettes passed through a glass wool filter to prevent sulphur (often present in the stock) from reaching the pump and interfering with the valve operation.

The product and raffinate receivers were 45-gal. drums fitted with sight-gauges The solvent receiver and reflux receiver were smaller mild steel drums also fitted with sight-gauges.

The lines and fittings were all of $\frac{1}{4}$-in., $\frac{3}{8}$-in., and $\frac{1}{2}$-in. I.P.S. mild steel. The globe valves were of iron, made by Jenkins Valve Co., Montreal.

The solvent rotameter was a standard Schutte-Koerting model.

Operation of the Pilot Plant

To start operating, crude mustard gas was fed into the column until it appeared in the sight-gauge (12 ft. from bottom of column). The solvent was then pumped in at a slow rate. As the interface began to rise the solvent rate was increased and the feed rate reduced. The flow rates were gradually adjusted to desired values and the interface kept at a definite level by adjusting the rate of removal of raffinate. Continuous operation was automatic, requiring minor adjustments to flow rates and temperatures. There was no trouble from plugging of lines by sulphur deposits. The raffinate flowed freely.

Results of Continuous Extraction Runs

Table III summarizes the data collected from data sheets for typical runs. The continuous extraction runs demonstrate the effect of varying flow rates, solvent dosage, and reflux ratio. The temperature of the column was kept at 25° C. for all runs. Table III includes calculated H.T.C.U. for the operating conditions used. For Run 17, the feed inlet was moved to the 24 ft. level.

TABLE III

PLANT OPERATIONAL DATA

Run No		2	6	8	9	10	14	17[1]
Duration of run (hr)		21	43	29	24	31	68	23
Reflux ratio		4/1	6/1	6/1	6/1	8/1	8/1	3 5/1
Feed rate, ml /min		100	30	50	70	40	43	50
Feed rate, lb /hr /sq ft		205 7	61 7	102 9	143 9	82 3	88 4	102 9
Solvent rate, ml /min		2000	670	910	1275	910	910	1025
Solvent rate, lb /hr /sq ft		1881	630	856	1200	856	856	965
Solvent dosage, lb solvent/lb feed		9 2	10 2	8 3	8 35	10 4	9 7	9 4
Crude mustard feed	M p , ° C	6 1	6 1	6 1	6 5	6 5	5 9	6 0
	Wt % *H* content by distillation	70 1	70 1	70 1	70 2	70 2	69 9	70 0
Extract product on solvent-free basis	% Total recovery	73 6	69 8	61 2	58 8	61 0	55 2	80 5
	% *H* recovery	87 2	86 0	77 7	74 4	80 6	72 2	94 2
	M p , ° C	9 0	9 9	10 9	10 4	12 0	11 6	8 7
	Wt % *H* content by distillation	83 1	86 0	89 1	87 5	92 5	91 3	82 2
% Solvent in product		4 3	4 4	4 2	4 4	4 1	4 6	4 3
Raffinate on solvent-free basis	% Total feed	25 8	32 0	39 4	40 2	38 2	46 3	20 0
	Wt % *H* content	32 9	29 8	38 7	49 3	39 2	45 2	19 5
% Solvent in raffinate		5 2	4 0	5 2	6 3	5 2	5 4	3 1
T C U's *m*		1 5	2 2	4 3	3 2	17 0	8 3	1 2
T C U's *n*		2 0	2 0	2 0	1 5	2 0	1 8	2 8
H T C U *m*		16	10 9	5 6	7 5	1 4	2 9	10 0
H.T C U *n*		6	6	6	8	6	6 7	8 6

[1] *Stripping section 24 ft*
Enriching section 12 ft.
H.T.C U = height of theoretical contact unit

Since the reflux enters at the top of the column a certain fraction of the enriching section is required for mixing. At the bottom the solvent must mix with the raffinate before equilibrium is approached and a portion of the stripping section is used for this purpose. The portion of the column used for mixing is unknown and as a result errors are introduced into calculation of the H.T.C.U.

The time required to reach equilibrium was different for the stripping section as compared to the enriching section. A product of constant melting point would appear in four hours, but the composition of the raffinate would not agree with its calculated value (related to the product) for as long as 24 hr.

The product, containing 4.0 to 4.5% solvent, varied in colour from pale yellow to almost colourless, depending on the purity. The iron and acid contents were negligible. There was a slight deposit of sulphur from extract products of high purity. Occasionally sulphur precipitated from the product in the product cooler, but never in sufficient quantities to cause trouble. This sulphur was most probably carried over by the solvent when high reflux ratios were used and remained in the product when the solvent was removed. Another source of sulphur would be the polysulphides, which may partially decompose on removal of the solvent at 100° C.

Discussion

Pilot plant operation has demonstrated that a maximum purity of approximately 92.5% can be obtained under extreme conditions of reflux, etc., as predicted by the equilibrium data.

An examination of Table III shows that only by accepting low yields and using reflux ratios of 8/1 was it possible to obtain a product approaching maximum purity (Runs 10 and 14). This indicates that the stripping section was of insufficient length to produce good stripping. In Run 17 when the stripping section was 24 ft. long the yield of available β,β'-dichlorodiethyl sulphide was 94%. The column was not long enough to give a product of maximum purity together with good yields.

It is to be noted that the H.T.C.U.-stripping seems to be much less affected by flow rates than the H.T.C.U. in the enriching section. Under favourable conditions (Runs 10 and 14) the H.T.C.U.-enriching is about 3 ft., while the H.T.C.U.-stripping is from 6 to 8 ft. in all the runs.

The complete assessment of the product depends on many factors, including storage trials in weapons. All that can be given here are the β,β'-dichlorodiethyl sulphide contents and melting points as listed in Table III.

Acknowledgment

The authors wish to acknowledge the valuable advice of Lt.-Col. E. A Flood and Major J. R. Dacey.

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THE ROTPROOFING EFFICACY OF MIXTURES OF METALLIC NAPHTHENATES[1]

By C. H. Bayley[2] and Muriel W. Weatherburn[2]

Abstract

The weathering characteristics of cotton duck treated with copper or zinc naphthenate containing mercury naphthenate or phenyl mercury naphthenate, and the effect of weathering on the rotproofing efficacy of these treatments as judged by the soil burial method, have been investigated. The presence of the mercury compounds reduced the loss of copper during burial and did not affect the weathering properties of the treated fabrics.

In an investigation of the rotproofing efficacy of binary mixtures, the naphthenates of cadmium, chromium, copper, iron, lead, mercury, silver, and zinc, containing a total of 0.2% metal, showed in general greater resistance to attack during soil burial than did samples containing the same percentage of metal in the form of single naphthenates. Ternary mixtures of the naphthenates of cadmium, copper, lead, mercury, silver, and zinc, applied to cotton fabric in equivalent concentration of total metal, were in general more effective than the binary mixtures of the same compounds.

Metallic naphthenates which have been used for the rotproofing of cellulosic textiles, cordage, etc., include chiefly those of copper and zinc. It has been found (6)* that the naphthenic acids used in the preparation of naphthenates impart considerable rot resistance to cotton fabrics. There is little doubt that this property of naphthenic acids contributes markedly to the usefulness as a rotproofer of such compounds as copper naphthenate in which the cation is itself a powerful fungicide. The amount of published information on other metallic naphthenates is limited and does not indicate any high degree of efficacy when these compounds are used singly.

Cadmium naphthenate has been reported (8) to be less effective than copper naphthenate. A commercial preparation containing iron naphthenate in conjunction with an aluminium compound and tar oils gave some protection when used on cotton fish nets, but was inferior to copper or zinc naphthenates (1). In tests with jute (4) mercury naphthenate was found to be inferior to copper naphthenate. Cotton duck treated with silver naphthenate in concentrations of 0.0084 and 0.0421% silver in Stoddard solvent solutions gave severe losses in breaking strength in a four weeks' soil burial test (7). Although these concentrations were of a very low order, it has been claimed (8) that silver compounds have no practical value as fungus inhibitors on fabric or cordage and that their efficiency is not sufficient to offset their cost. However, in another investigation (5) silver naphthenate in conjunction with chlorinated rubber and a plasticizer gave promising results on linen twine subjected to sea immersion.

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Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1531.

[2] *Chemist.*

* *And unpublished data, National Research Laboratories, Ottawa.*

In a previous publication (2) it had been shown that the addition of small quantities of mercury naphthenate to copper naphthenate improved greatly the efficacy of the latter compound in inhibiting the growth on unbleached cotton duck of the surface growing fungus *Aspergillus niger* and a cellulose destroying species of *Penicillium*. The data given in this paper comprise the results of two further studies. The first of these covers an extension of the previous work to a study of the comparative rotproofing efficacy, as judged by soil burial and resistance to weathering, of phenyl mercury naphthenate and mercury naphthenate in admixture with copper and zinc naphthenates, respectively. Secondly, the rotproofing efficacy as measured by the soil burial test was determined for other metallic naphthenates, viz., those of cadmium, chromium, copper, iron, lead, mercury, silver, and zinc, in binary mixtures containing equal concentrations of the metals, and, with the exception of chromium and iron, in ternary mixtures containing equal concentrations of metals. The single naphthenates were included as controls.

A. Materials and Methods

The metallic naphthenates used were prepared by Nuodex Products Inc., Elizabeth, N.J., U.S.A., or by Nuodex Products of Canada Ltd., Leaside (Toronto), Ont., and were obtained through the latter firm. They contained the percentages of metal shown, viz.: cadmium 8.10, chromium 7.95, copper 8.10, iron 6.06, lead 23.93, mercury 24.90, phenyl mercury 10.08, silver 8.20, and zinc 8.18.

The fabrics used were unbleached cotton army ducks weighing 10 and 12 oz. per sq. yd., and a No. 8 unbleached duck of 18 oz. per sq. yd. Throughout this paper these ducks are referred to as '10 oz.', '12 oz.', and '18 oz.' ducks, respectively.

The treatments were applied from solutions in Stoddard solvent as previously described (2). In the treatments involving zinc naphthenate mixed with mercury naphthenate and phenyl mercury naphthenate respectively, a wax waterproofing compound consisting of a mixture of paraffin wax and petrolatum (3) was incorporated in the treating solution to give approximately 10% of the mixture on the dry weight of the treated fabric.

In the study of the effect of weathering and of soil burial on copper and zinc naphthenates in the presence of mercury compounds the percentage of copper in the copper naphthenate treated samples was 0.20, the mercury compounds being present in amounts corresponding to 0.005, 0.01, 0.03, and 0.05% mercury; the percentage of zinc in the samples treated with zinc naphthenate was 0.79, the mercury compounds being present in amounts corresponding to 0.01 and 0.05% mercury. All percentages of metal are calculated on the basis of the dry treated sample, the copper and zinc being determined as described previously (9, 10).

The samples used in studying the effect of binary mixtures of metallic naphthenates contained approximately 0.1% of each metal in the form of naphthenates, the control samples (one metal only) containing 0.1 and 0.2% metal. With the samples containing ternary mixtures of naphthenates the total content of metal was 0.2% as above, the content of each metal being approximately 0.07%, the control samples being as described above. The percentages of metal shown were calculated on the dry weight of the treated fabric and were obtained from the wet pick-up data.

The details of the leaching, soil burial, weathering, and breaking strength techniques employed, and also the record of weather conditions during the exposure period, have been given in an earlier paper (3). In certain cases an estimate of microbiological attack occurring during soil burial was made on the basis of an arbitrary system of growth ratings (*A* to *F*) obtained independently by three observers. It was found that the observations so obtained were sufficiently uniform to permit this system of rating to be used in judging the extent of microbiological attack without the necessity of carrying out breaking strength measurements. The ratings used were as follows:

A—No growth.

B—Very slight surface growth.

C—Moderate growth but not over whole surface; fabric remains strong to pulling by hand.

D—Heavy growth over whole surface; noticeable weakening of fabric.

E—Very heavy growth over whole surface with noticeable thinning of fabric and possible development of holes.

F—Fabric partially or entirely disintegrated.

B. Experimental Results

1. *Effect of Mercury Compounds on the Soil Burial and Weathering Characteristics of Copper and Zinc Naphthenate Treated Samples*

Table I gives the data showing the effect of soil burial on loss in breaking strength and copper content of 18 oz. cotton duck treated with mixtures of copper naphthenate and mercury naphthenate, or phenyl mercury naphthenate. The effect of soil burial, weathering, and weathering followed by soil burial, on loss in breaking strength of 12 oz. cotton duck similarly treated is shown in Table II. Table III gives similar data for 10 oz. duck treated with zinc naphthenate and the two above-mentioned mercury compounds.

(*a*) *Burial Effects*

It will be apparent from the data in Table I that the samples of duck treated with the mercury compounds alone showed little or no resistance to rotting. The sample treated with copper naphthenate alone (0.20% copper) showed a

TABLE I

EFFECT OF BURIAL ON THE BREAKING STRENGTH AND COPPER CONTENT OF 18 OZ. COTTON DUCK TREATED WITH COPPER NAPHTHENATE PLUS MERCURY NAPHTHENATE OR PHENYL MERCURY NAPHTHENATE

Original metal concentration, %		Decrease in breaking strength, % of orig.				Decrease in copper content, % of orig.			
		Mercury naphthenate		Phenyl mercury naphthenate		Mercury naphthenate		Phenyl mercury naphthenate	
Copper	Mercury	Leached 24 hr. and buried		Leached 24 hr. and buried		Leached 24 hr. and buried		Leached 24 hr. and buried	
		2 wk.	4 wk.	2 wk.	4 wk.	2 wk.	4 wk.	2 wk.	4 wk.
0.20	0.005	6	38	7	32	25	20	20	23
0.20	0.01	0	28	8	10	—	15	23	23
0.20	0.03	5	5	+2	5	30	20	20	20
0.20	0.05	0	8	12	4	—	15	20	20
Controls									
0	0.005	78	—	71	—	—	—	—	—
0	0.01	88	—	78	—	—	—	—	—
0	0.03	92	—	87	—	—	—	—	—
0	0.05	84	—	83	—	—	—	—	—
0.20	0	30	64	—	—	50	64	—	—

TABLE II

EFFECT OF OUTDOOR WEATHERING AND BURIAL ON THE BREAKING STRENGTH OF 12 OZ. COTTON DUCK TREATED WITH COPPER NAPHTHENATE PLUS MERCURY NAPHTHENATE OR PHENYL MERCURY NAPHTHENATE

Original metal concentration, %		Decrease in breaking strength, % of original									
		Mercury naphthenate					Phenyl mercury napthenate				
Copper	Mercury	Weath. 4 mo.	Weathered 4 mo. and buried		Buried 4 wk.	Leached 24 hr. and buried 4 wk.	Weath. 4 mo.	Weathered 4 mo. and buried		Buried 4 wk.	Leached 24 hr. and buried 4 wk.
			2 wk.	4 wk.				2 wk.	4 wk.		
0.26	0.005	36	50	97	27	37	31	57	—	15	10
0.26	0.01	37	65	96	28	31	36	49	—	14	17
0.26	0.03	35	54	96	17	31	32	55	—	16	31
0.26	0.05	39	64	95	5	16	34	49	—	—	8
Controls											
0	0.005	34	93	93	—	—	39	75	—	—	—
0	0.01	32	90	97	—	—	40	76	—	—	—
0	0.03	39	87	97	—	—	40	—	—	—	—
0	0.05	29	83	93	—	—	41	—	—	—	—
0.26	0	36	54	96	35	76	—	—	—	—	—
0	0	42	—	—	—	—	—	—	—	—	—

TABLE III

EFFECT OF OUTDOOR WEATHERING AND BURIAL ON THE BREAKING STRENGTH OF 10 OZ. COTTON DUCK TREATED WITH ZINC NAPHTHENATE PLUS MERCURY NAPHTHENATE OR PHENYL MERCURY NAPHTHENATE AND WAX

Original metal concentration, %		Decrease in breaking strength, % of original											
		Mercury naphthenate						Phenyl mercury naphthenate					
Zinc	Mercury	Weath. 4 mo.	Weath. 4 mo. and buried		Buried 2 wk.	Leached 24 hr. and buried		Weath. 4 mo.	Weath. 4 mo. and buried		Buried 2 wk.	Leached 24 hr. and buried	
			2 wk.	4 wk.		2 wk.	4 wk.		2 wk.	4 wk.		2 wk.	4 wk.
Without wax													
0.79	0.01	43	79	97	9	1	83	44	84	98	+16	+1	97
0.79	0.05	47	85	97	+7	6	86	46	90	97	14	+7	96
Controls													
0	0.05	47	81	—	100	100	—	—	—	—	—	—	—
0.79	0	38	81	96	20	27	93	—	—	—	—	—	—
0	0	41	89	—	98	100	—	—	—	—	—	—	—
With wax													
0.79	0 01	66	82	97	1	+6	74	68	77	98	+6	+8	74
0.79	0 05	67	81	97	7	+1	38	63	72	98	9	7	41
Controls													
0.79	0	68	82	97	8	17	82	—	—	—	—	—	—
0	0	69	87	—	100	100	—	—	—	—	—	—	—

breaking strength loss of 30 and 64% after leaching followed by two and four weeks' burial, respectively. The addition of the mercury compounds reduced these losses to an insignificantly low level. Similar breaking strength effects were observed with the 12 oz. duck (Table II), the best resistance to soil burial being shown by the copper treated sample containing 0.05% mercury. The presence of the mercury compounds likewise reduced the strength losses resulting from soil burial in the samples treated with zinc naphthenate (Table III).

It is of interest to note that the loss of copper during soil burial (Table I) was considerably less in the presence of the mercury compounds. This is probably due to the effect of the latter compounds in reducing the activity of copper tolerant organisms, many of which are known to bring about solubilization and consequent loss by leaching of copper compounds.

(b) Weathering Effects

It will be noted that with the samples treated with copper and mercury naphthenates either singly or in mixtures (Table II), or with zinc and mercury naphthenates (Table III), there was no evidence of increased breaking strength losses over that shown by the untreated control on weathering.

In this series the increased breaking strength losses shown by the waxed samples substantiate previous data covering the use of the same wax compound (3). Further investigation has shown that this effect is due largely or entirely to the petrolatum constituent. The mercury compounds had no effect on the breaking strength losses of copper naphthenate or zinc naphthenate treated samples followed by soil burial. It has previously been shown (3) that mercury naphthenate and zinc naphthenate are readily removed by weathering for four months, and this explains the lack of efficiency with respect to rotproofing after weathering.

2. *Effect of Soil Burial on Samples Treated with Binary and Ternary Mixtures of Metallic Naphthenates*

Tables IV, VI, VIII, and X give growth rating data for binary and ternary mixtures of the various metallic naphthenates after leaching followed by burial for two and four weeks, respectively. The data given in Tables V, VII, IX, and XI show the frequency of occurrence of growth ratings for various metallic radicles when used as single naphthenates or binary mixtures of naphthenates (Tables V and VII) or ternary mixtures of naphthenates (Tables IX and XI).

TABLE IV

GROWTH RATING OF 10 OZ. COTTON DUCK TREATED WITH METALLIC NAPHTHENATES, SINGLY (0.1 and 0.2% METAL ON FABRIC) AND IN BINARY MIXTURES (0.1% OF EACH METAL ON FABRIC) AFTER BURIAL FOR TWO WEEKS WITH PRELIMINARY LEACHING

Metallic naphthenate (0 1% metal)	Metallic naphthenate (0.1% metal) in combination with metallic naphthenate (0 1% metal) in left-hand column							
	Cadmium	Chromium	Copper	Iron	Lead	Mercury	Silver	Zinc
—	*D*	*D*	*C-D*	*D-E*	*E*	*D*	*D*	*D*
Cadmium	**C**	*D*	*B*	*D*	*C*	*A*	*C*	*C*
Chromium	*D*	**D**	*D*	*E*	*E*	*B*	*E*	*D*
Copper	*B*	*D*	**B**	*D*	*D*	*A*	*B*	*C*
Iron	*D*	*E*	*D*	**E**	*D*	*B*	*D*	*D*
Lead	*C*	*E*	*D*	*D*	**D**	*B*	*D*	*C*
Mercury	*A*	*B*	*A*	*B*	*B*	**B**	*B*	*B*
Silver	*C*	*E*	*B*	*D*	*D*	*B*	**D**	C
Zinc	*C*	*D*	*C*	*D*	*C*	*B*	*C*	**D**

The growth ratings for samples treated with single naphthenates and with binary mixtures of naphthenates and subjected to soil burial for two weeks with preliminary leaching (Table IV) show that copper and mercury when used singly (0.2% metal) gave marked resistance to microbiological attack; cadmium gave moderate resistance, whereas the other compounds gave little

TABLE V

FREQUENCY OF OCCURRENCE OF GROWTH RATINGS FOR VARIOUS METALLIC RADICLES WHEN USED AS SINGLE NAPHTHENATES (0.2% METAL ON FABRIC) OR IN BINARY MIXTURES OF NAPHTHENATES (0.1% OF EACH METAL ON FABRIC), AFTER BURIAL FOR TWO WEEKS WITH PRELIMINARY LEACHING

Metallic radicle	*A*		*B*		*C*		*D*		*E*		*F*	
	1[1]	2[2]	1	2	1	2	1	2	1	2	1	2
Cadmium	—	1	—	1	1	3	—	2	—	—	—	—
Chromium	—	—	—	1	—	—	1	3	—	3	—	—
Copper	—	1	1	2	—	1	—	3	—	—	—	—
Iron	—	—	—	1	—	—	—	5	1	1	—	—
Lead	—	—	—	1	—	2	1	3	—	1	—	—
Mercury	—	2	1	5	—	—	—	—	—	—	—	—
Silver	—	—	—	2	—	2	1	2	—	1	—	—
Zinc	—	—	—	1	—	4	1	2	—	—	—	—
Total occurrence	0	4	2	14	1	12	4	20	1	6	0	0
% of possible occurrence	0	7	25	25	13	21	50	36	13	11	0	0

[1] *Single compound.*

[2] *Binary mixture of compounds.*

TABLE VI

GROWTH RATING OF 10 OZ. COTTON DUCK TREATED WITH METALLIC NAPHTHENATES, SINGLY (0.1 AND 0.2% METAL ON FABRIC) AND IN BINARY MIXTURES (0.1% OF EACH METAL ON FABRIC) AFTER BURIAL FOR FOUR WEEKS WITH PRELIMINARY LEACHING

Metallic naphthenate (0.1% metal)	Metallic naphthenate (0.1% metal) in combination with metallic naphthenate (0.1% metal) in left-hand column							
	Cadmium	Chromium	Copper	Iron	Lead	Mercury	Silver	Zinc
—	*E*	*F*	*E*	*F*	*F*	*F*	*F*	*F*
Cadmium	**D**	*E*	*D*	*E*	*E*	*D*	*C*	*E*
Chromium	*E*	**F**	*E*	*F*	*F*	*E*	*E*	*F*
Copper	*D*	*E*	**D**	*E*	*E*	*B*	*C*	*E*
Iron	*E*	*F*	*E*	**F**	*F*	*F*	*E*	*F*
Lead	*E*	*F*	*E*	*F*	**F**	*F*	*F*	*F*
Mercury	*D*	*E*	*B*	*F*	*F*	**E**	*E*	*E*
Silver	*C*	*E*	*C*	*E*	*F*	*E*	**F**	*C*
Zinc	*E*	*F*	*E*	*F*	*F*	*E*	*C*	**E**

or no resistance. A comparison of the over-all effectiveness of the compounds is given in Table V, in which the frequency of occurrence of the six growth ratings are shown for the single and binary mixture treatments. It will be noted that, based on the percentage of possible occurrence, 25% of the single compounds and 32% of the binary mixtures gave growth ratings of *A* or *B*. Including the ratings for moderate growth (rating *C*) which embraces those

TABLE VII

FREQUENCY OF OCCURRENCE OF GROWTH RATINGS FOR VARIOUS METALLIC RADICLES WHEN USED AS SINGLE NAPHTHENATES (0.2% METAL ON FABRIC) OR IN BINARY MIXTURES OF NAPHTHENATES (0.1% OF EACH METAL ON FABRIC), AFTER BURIAL FOR FOUR WEEKS WITH PRELIMINARY LEACHING

Metallic radicle	*A*		*B*		*C*		*D*		*E*		*F*	
	1[1]	2[2]	1	2	1	2	1	2	1	2	1	2
Cadmium	—	—	—	—	—	1	1	2	—	4	—	—
Chromium	—	—	—	—	—	—	—	—	—	4	1	3
Copper	—	—	—	1	—	1	1	2	—	3	—	—
Iron	—	—	—	—	—	—	—	—	—	3	1	4
Lead	—	—	—	—	—	—	—	—	—	2	1	5
Mercury	—	—	—	1	—	—	—	1	1	3	—	2
Silver	—	—	—	—	—	3	—	—	—	3	1	2
Zinc	—	—	—	—	—	1	—	1	1	2	—	3
Total occurrence	0	0	0	2	0	6	2	6	2	24	4	18
% of possible occurrence	0	0	0	4	0	11	25	11	25	43	50	32

[1] *Single compound.*

[2] *Binary mixture of compounds.*

TABLE VIII

GROWTH RATING OF 10 OZ. COTTON DUCK TREATED WITH METALLIC NAPHTHENATES, SINGLY (0.2% METAL ON FABRIC) AND IN TERNARY MIXTURES (0.07% OF EACH METAL ON FABRIC) AFTER BURIAL FOR TWO WEEKS WITH PRELIMINARY LEACHING

Metallic naphthenate	Metallic naphthenates in mixture with metallic naphthenate in left-hand column (total concentration on fabric = 0.2% metal)																				
	Cadmium plus						Copper plus					Lead plus				Mercury plus			Silver plus		Zinc plus
	Cd	Cu	Pb	Hg	Ag	Zn	Cu	Pb	Hg	Ag	Zn	Pb	Hg	Ag	Zn	Hg	Ag	Zn	Ag	Zn	Zn
Cadmium	**D**	—	—	—	—	—	—	*C*	*A*	*C*	*B*	—	*A*	*C*	*D*	—	*A*	*C*	—	*C*	—
Copper	—	—	*C*	*A*	*C*	*B*	**C**	—	—	—	—	—	*B*	*C*	*D*	—	*B*	*A*	—	*C*	—
Lead	—	*C*	—	*A*	*C*	*D*	—	—	*B*	*C*	*D*	**D**	—	—	—	—	*C*	*B*	—	*C*	—
Mercury	—	*A*	*A*	—	*A*	*C*	—	*B*	—	*B*	*A*	—	—	*C*	*B*	**C**	—	—	—	*B*	—
Silver	—	*C*	*C*	*A*	—	*C*	—	*C*	*B*	—	*C*	—	*C*	—	*C*	—	—	*B*	**D**	—	—
Zinc	—	*B*	*D*	*C*	*C*	—	—	*D*	*A*	*C*	—	—	*B*	*C*	—	—	*B*	—	—	—	**D**

samples that did not show significant loss of strength, the percentages are 38 and 53 for the single compounds and the binary mixtures, respectively.

Considering the various metals it will be noted that mercury gave the best over-all performance, showing no growth when mixed with cadmium or copper and only slight surface growth in admixture with the other metals. The order of decreasing efficiencies for the other metals in binary mixtures was: copper, cadmium, silver, zinc, lead, chromium, and iron.

The data for the four week burial of the same samples (Table VI) show that in all cases the samples treated with the single compounds gave growth ratings

TABLE IX

FREQUENCY OF OCCURRENCE OF GROWTH RATINGS FOR VARIOUS METALLIC RADICLES WHEN USED AS SINGLE NAPHTHENATES (0.2% METAL ON FABRIC) OR IN TERNARY MIXTURES OF NAPHTHENATES (0.07% OF EACH METAL ON FABRIC) AFTER BURIAL FOR TWO WEEKS WITH PRELIMINARY LEACHING

Metallic radicle	*A*		*B*		*C*		*D*		*E*		*F*	
	1[1]	3[2]	1	3	1	3	1	3	1	3	1	3
Cadmium	—	3	—	1	1	5	1	1	—	—	—	—
Copper	—	2	—	3	—	4	—	1	—	—	—	—
Lead	—	1	—	2	1	5	—	2	—	—	—	—
Mercury	—	4	—	4	1	2	—	—	—	—	—	—
Silver	—	1	—	2	—	7	1	—	—	—	—	—
Zinc	—	1	—	3	—	4	1	2	—	—	—	—
Total occurrence	0	12	0	15	3	27	3	6	0	0	0	0
% of possible occurrence	0	20	0	25	50	45	50	10	0	0	0	0

[1] *Single compound.*

[2] *Ternary mixture of compounds.*

TABLE X

GROWTH RATING OF 10 OZ. COTTON DUCK TREATED WITH METALLIC NAPHTHENATES, SINGLY (0.2% METAL ON FABRIC), IN BINARY MIXTURES (0.1% OF EACH METAL ON FABRIC) AND TERNARY MIXTURES (0.07% OF EACH METAL ON FABRIC) AFTER BURIAL FOR FOUR WEEKS WITH PRELIMINARY LEACHING

Metallic naphthenate	Metallic naphthenates in mixture with metallic naphthenate in left-hand column (total concentration on fabric = 0 2% metal)																				
	Cadmium plus						Copper plus					Lead plus				Mercury plus			Silver plus		Zinc plus
	Cd	Cu	Pb	Hg	Ag	Zn	Cu	Pb	Hg	Ag	Zn	Pb	Hg	Ag	Zn	Hg	Ag	Zn	Ag	Zn	Zn
—	**E**	*D*	*E*	*F*	*E*	*F*	**D**	*E*	*D*	*C*	*E*	**F**	*F*	*F*	*F*	**F**	*F*	*F*	**F**	*F*	**E**
Cadmium	**E**	—	—	—	—	—	—	*E*	*D*	*E*	*D*	—	*F*	*E*	*E*	—	*B*	*F*	—	*D*	—
Copper	—	—	*E*	*D*	*E*	*D*	**D**	—	—	—	—	—	*F*	*D*	*F*	—	*C*	*E*	—	*D*	—
Lead	—	*E*	—	*F*	*E*	*E*	—	—	*F*	*D*	*F*	**F**	—	—	—	—	*F*	*F*	—	*F*	—
Mercury	—	*D*	*F*	—	*B*	*F*	—	*F*	—	*C*	*E*	—	—	*F*	*F*	**F**	—	—	—	*F*	—
Silver	—	*E*	*E*	*B*	—	*D*	—	*D*	*C*	—	*D*	—	*F*	—	*F*	—	—	*F*	**F**	—	—
Zinc	—	*D*	*E*	*F*	*D*	—	—	*F*	*E*	*D*	—	—	*F*	*F*	—	—	—	—	—	—	**E**

of *D* or poorer, although it was noted that with the cadmium and with the copper treated samples the growth while heavy was not as intense as with the other compounds. The most effective treatment was the mercury–copper mixture, while mixtures of silver with copper and with cadmium or zinc were moderately effective. From the data for frequency of occurrence of the various ratings (Table VII), it will be noted that approximately 15% of the binary mixtures showed ratings of *C* or better, whereas none of the single compounds showed ratings better than *D*.

TABLE XI

FREQUENCY OF OCCURRENCE OF GROWTH RATINGS FOR VARIOUS METALLIC RADICLES WHEN USED AS SINGLE NAPHTHENATES (0.2% METAL ON FABRIC), IN BINARY MIXTURES (0.1% OF EACH METAL ON FABRIC), AND TERNARY MIXTURES (0.07% OF EACH METAL ON FABRIC) AFTER BURIAL FOR FOUR WEEKS WITH PRELIMINARY LEACHING

Metallic radicle	*A*			*B*			*C*			*D*			*E*			*F*		
	1[1]	2[2]	3[3]	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Cadmium	—	—	—	—	—	1	—	—	—	—	1	3	1	2	4	—	2	2
Copper	—	—	—	—	—	—	—	1	1	1	3	4	—	1	3	—	—	2
Lead	—	—	—	—	—	—	—	—	—	—	1	1	—	1	3	1	3	6
Mercury	—	—	—	—	—	1	—	—	1	—	1	1	—	—	1	1	4	6
Silver	—	—	—	—	—	1	—	1	1	—	—	3	—	1	2	1	3	3
Zinc	—	—	—	—	—	—	—	—	—	—	—	3	1	1	2	—	4	5
Total occurrence	0	0	0	0	0	3	0	2	3	1	6	15	2	6	15	3	16	24
% of possible occurrence	0	0	0	0	0	5	0	7	5	17	20	25	33	20	25	50	53	40

[1] *Single compound.*

[2] *Binary mixture of compounds.*

[3] *Ternary mixture of compounds.*

Owing to the relatively poor performance of the chromium and iron compounds in the above investigation they were omitted from the subsequent study dealing with ternary mixtures. In this study, control tests using fabric treated with single compounds subjected to a two week burial period, and also binary mixtures subjected to a four week burial period, were run simultaneously to provide a basis of comparison with the first series. The data obtained with these controls suggest that the soil used in the second series was somewhat more active than that used in the first series. The data indicate that for a two week burial period (Tables VIII and IX), the ternary mixtures were considerably more effective than the single compounds. It will be noted that the percentage of possible occurrence of growth ratings of *C* or better was 90% for the ternary mixtures, compared with 50% for the single compounds. Ternary mixtures on fabrics that showed no growth were: mercury–cadmium–copper, mercury–cadmium–lead, mercury–cadmium–silver, and mercury–copper–zinc. Very slight growth was shown by fabric treated with copper–cadmium–zinc, mercury–copper–silver, mercury–lead–zinc, and mercury–silver–zinc. The data for the fabric containing ternary mixtures and subjected to a four week burial period (Tables X and XI) indicate that these mixtures were on the whole more effective than the binary mixtures, and these in turn were more effective than the single compounds. The only treatment showing a *B* rating was the mercury–cadmium–silver mixture. All other treatments gave ratings of *C* or less.

The effectiveness of certain of the binary and ternary mixtures compared with the corresponding single compounds is illustrated in Figs. 1 to 9.

C. Colour of Treated Fabrics

Since the colour imparted to fabrics by rotproofing treatments is of interest to the textile trade, the following data on the colours of the treated fabrics used in this investigation are given. For the single treatments in concentration of 0.2% metal, the colours of the treated samples were as follows: copper—medium blue green; silver—rose purple; chromium—bluish grey; iron—cream; cadmium, lead, mercury, and zinc—colourless.

All binary mixtures containing silver ranged in shade from light rose to mauve. Those containing copper were pale bluish green, with the exception of copper plus silver, which was mauve. All other mixtures were either light grey, cream, or colourless.

Ternary mixtures were pale green in the presence of copper, all others being either very pale rose or colourless.

It would be expected that in higher concentrations there would be a deepening in the shade of the coloured samples.

It is of interest to note that certain binary or ternary mixtures (e.g., cadmium–mercury, cadmium–mercury–lead, and cadmium–mercury–silver) provided treatments that were nearly colourless and that had rotproofing efficacies superior to that of copper naphthenate used singly.

Acknowledgments

The authors wish to acknowledge with thanks the kindness of Nuodex Products Inc., Elizabeth, N.J., U.S.A., and Nuodex Products of Canada Ltd., Leaside (Toronto), Ont., for providing supplies of the naphthenates used in this investigation; also to Miss E. E. Raphael and Messrs. H. S. Quinn and B. H. Pout for assistance in carrying out the work.

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(Figs. 1 to 9 follow.)

PLATE I

FIGS. 1-5. *Binary mixtures of naphthenates on 10 oz. cotton duck, leached 24 hr., buried for two and four weeks.*

FIG. 1. *Silver and zinc—(buried two weeks)*
Left —Silver (0.1%) + zinc (0.1%)
Centre—Silver (0.2%)
Right —Zinc (0.2%)

FIG. 2. *Silver and zinc—(buried four weeks)*
Left —Silver (0.1%) + zinc (0.1%)
Centre—Silver (0.2%)
Right —Zinc (0.2%)

FIG. 3. *Copper and mercury—(buried four weeks)*
Left —Copper (0.1%) + mercury (0.1%)
Centre—Copper (0.2%)
Right —Mercury (0.2%)

FIG. 4. *Copper and silver—(buried four weeks)*
Left —Copper (0.1%) + silver (0.1%)
Centre—Copper (0.2%)
Right —Silver (0.2%)

FIG. 5. *Cadmium and silver—(buried four weeks)*
Left —Cadmium (0.1%) + silver (0.1%)
Centre—Cadmium (0.2%)
Right —Silver (0.2%)

PLATE II

FIGS. 6 and 7. *Ternary mixtures of naphthenates on 10 oz. cotton duck, leached 24 hr. and buried two weeks.*

FIG. 6. *Copper, cadmium, and zinc—*
From left to right
Copper (0.07%) + cadmium (0.07%) + zinc (0 07%);
Copper (0.2%); cadmium (0 2%); zinc (0.2%).

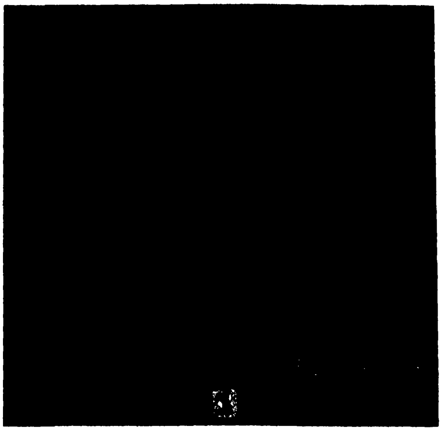
FIG. 7. *Mercury, lead, and zinc—*
From left to right
Mercury (0 07%) + lead (0.07%) + zinc (0.07%);
Mercury (0.2%); lead (0.2%); zinc (0.2%).

PLATE III

FIGS. 8 and 9. *Ternary mixtures of naphthenates on 10 oz. cotton duck, leached 24 hr. and buried two weeks.*

FIG. 8. *Mercury, silver, and zinc—*
From left to right
Mercury (0.07%) + silver (0 07%) + zinc (0.07%);
Mercury (0.2%); silver (0.2%); zinc (0.2%).

FIG. 9. *Cadmium, mercury, and silver—*
From left to right
Cadmium (0.07%) + mercury (0.07%) + silver (0.07%);
Cadmium (0.2%); mercury (0.2%); silver (0.2%).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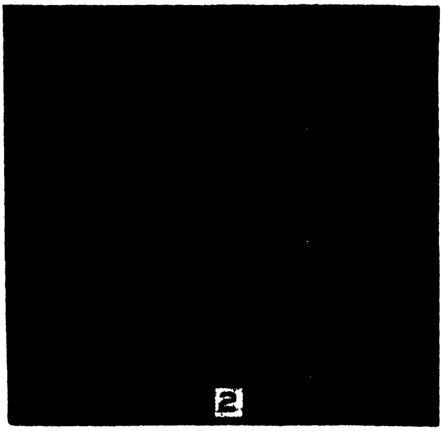
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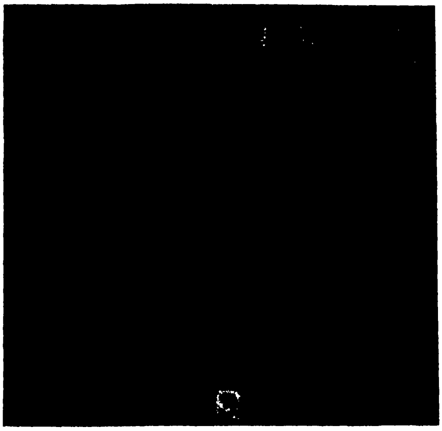
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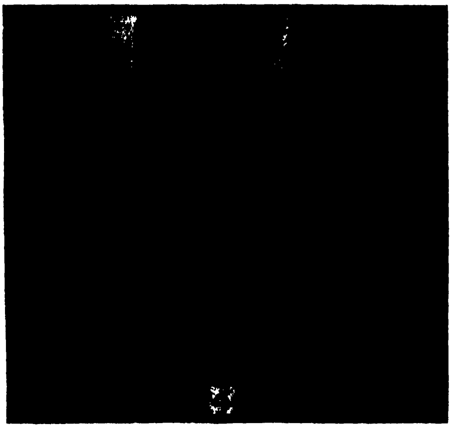
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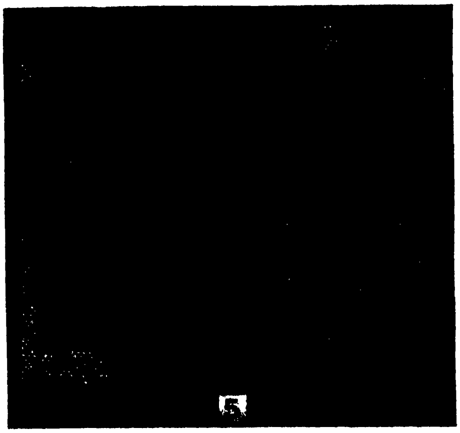
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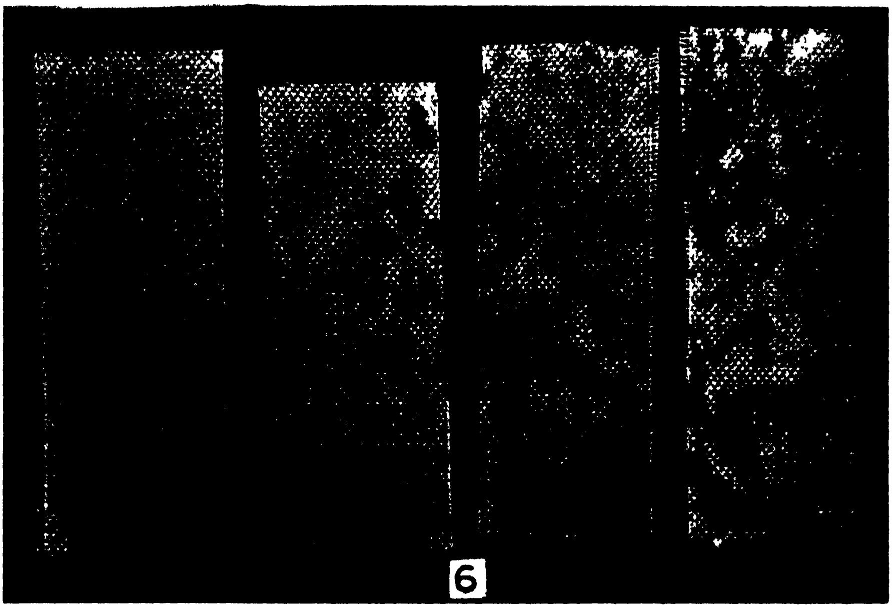
PLATE II



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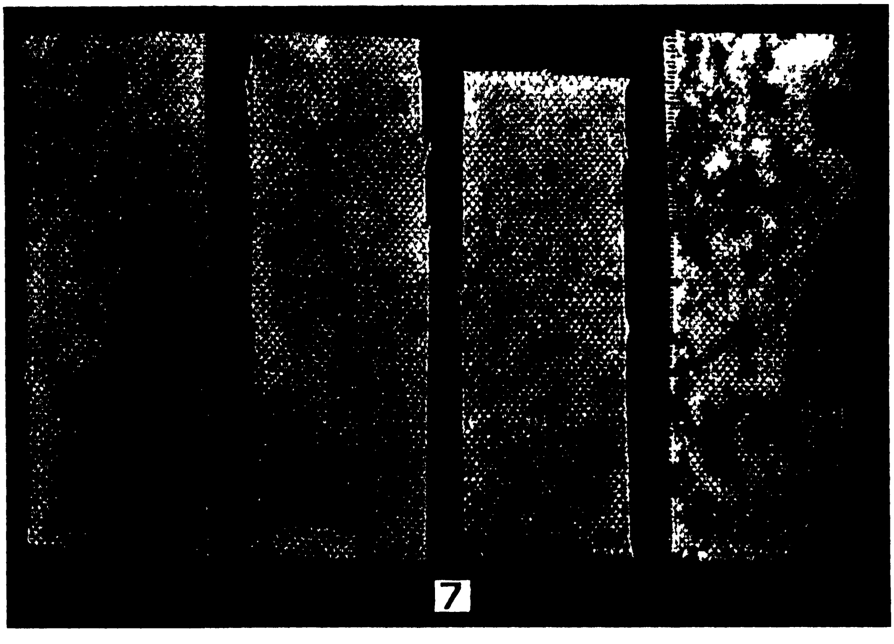

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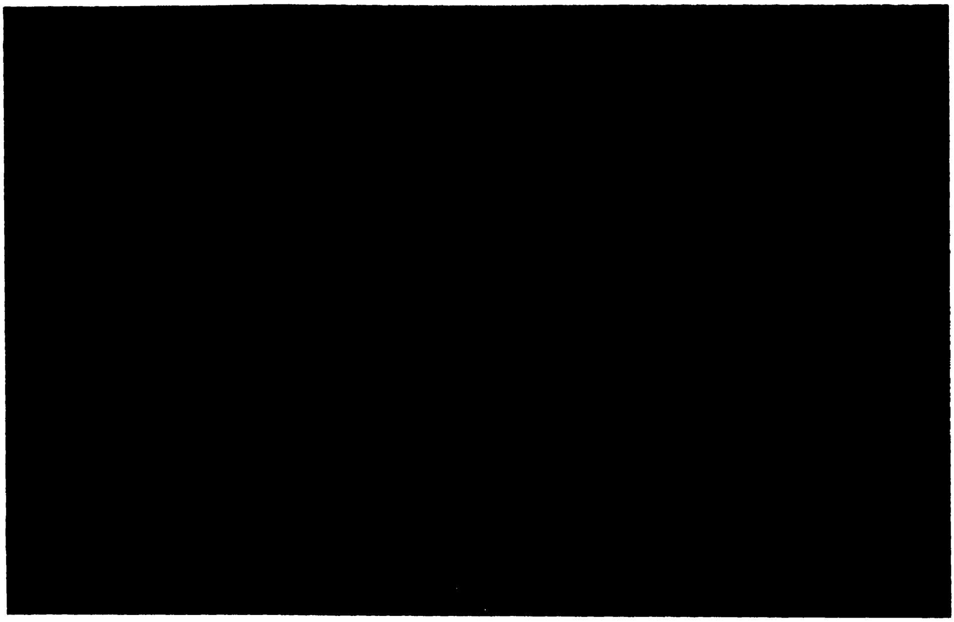
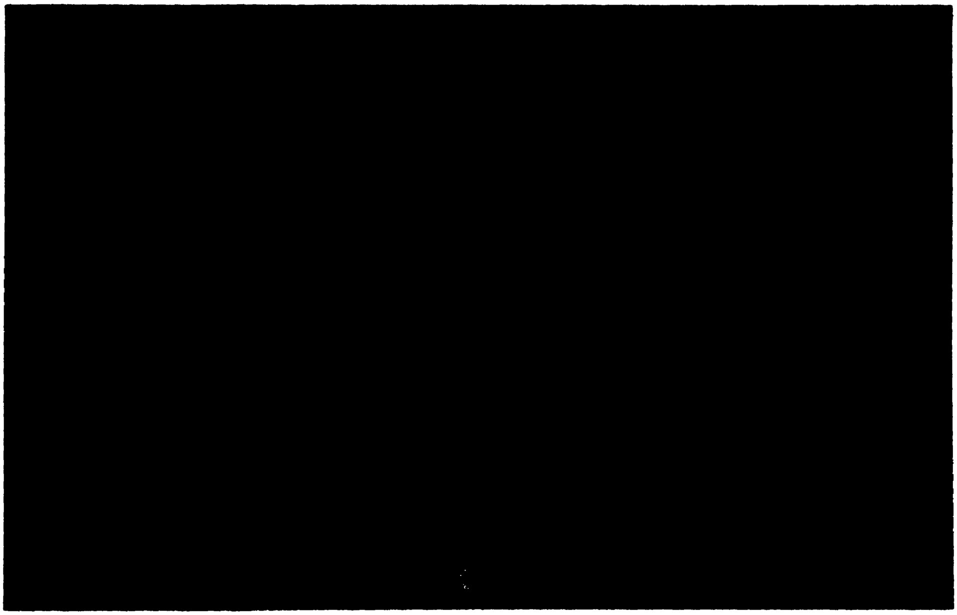
PLATE III





AN APPARATUS FOR THE BUTT-WELDING OF FINE WIRES[1]

BY L. D. ARMSTRONG[2] AND T. M. DAUPHINEE[2]

Abstract

A butt-welding apparatus employing a condenser discharge is described. This apparatus was developed for welding thermocouples of small dimensions but is suitable for most types of fine wires. The welding characteristics and possible applications are given in detail.

During a recent investigation of the thermal conductivity of metals it was necessary to weld a large number of fine wires of several different materials. For this purpose flame welding was inconvenient and the finished joints were not always satisfactory; in particular, the resultant joint was almost always considerably larger in diameter than the original wires, and for some applications this was highly undesirable. In addition, flame welding could not be used with certain materials. In order to overcome these difficulties a method of butt-welding by means of an electrical discharge was developed, and it proved to be very satisfactory.

Apparatus

In order to obtain an apparatus in which the time of heating would be kept short and in which, thereby, the extent of the wire heated and the amount of oxidation would both be kept to a minimum, the energy for the welding was obtained from the discharge of a bank of condensers. This principle of a condenser discharge has been used in the spot welder of Copeland and Rothschild (1), and to some extent commercially. The successful operation of the apparatus as finally developed depends on a suitable adjustment of four variable quantities; viz., capacity, potential, resistance, and polarity.

A photograph of the apparatus is shown in Fig. 1 and a schematic diagram of the electrical circuit in Fig. 3. The condensers (*a*) are connected through switches (*b*) in such a way that any capacity between 5 and 600 μf. can be selected, and are charged to the desired potential by means of a 300 v. power supply (*c*) connected across a potentiometer (*d*). The discharge passes to the welding clips (*e*) through a push-button switch (*f*) and an adjustable series resistance (*g*), which serves to vary the time constant of the discharge. A reversing switch (*h*) changes the polarity on the clips. The wires to be welded are clamped in the spring jaws of the clips, one of which is fastened rigidly to the base of the apparatus, while the other is mounted in such a way that it can be moved in three mutually perpendicular directions, two of them in the focal plane of the viewing microscope (Fig. 2). By this arrangement the position of one wire relative to the other can be easily and accurately adjusted.

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[2] *Physicist.*

Method

The method of butt-welding the wires is, briefly, as follows. The wires, the ends of which have previously been cut off with a sharp edge, are placed in the clips and aligned in the field of the microscope. The circuit constants (capacity, potential, resistance, and polarity) having been set to the values required for the specific size and type of wires, the two wires are brought together, with the push-button switch closed. The resultant spark discharge melts the ends of the wires into two ball-like tips, the appearance and size of which depend on the circuit constants. After any necessary adjustments have been made, the tips are brought together again, when, depending on the material of the wires, either the weld takes place or the two balls stick together. If the latter occurs, the balls are pulled apart and the weld is completed on the next approach. Photographs showing successive stages of the welding process are shown in Fig. 4.

The values of the circuit constants used are quite critical and have been experimentally determined for the particular wire combinations. Some representative values for different types of welds are given in Table I. The apparatus as designed at present is not suitable for welding wires larger than No. 28 B. & S. gauge. All the common wire materials have been welded successfully (alumel, chromel, constantan, copper, gold, manganin, nickel, and platinum) although difficulty has been encountered in welding tungsten.

TABLE I

EXAMPLES OF CIRCUIT CONSTANTS FOR TYPICAL WELDS

Clip No. 1	Clip No. 2	Capacity, μf.	Potential, v.	Resistance, ohms	Polarity	Description
0.003 in. platinum	0.003 in. platinum	10	225	¼	—	Weld on third approach
0.005 in. platinum	0.005 in. platinum	70	140	3	—	Same as above
0.005 in. platinum	0.003 in. platinum	40	120	0	No. 2 pos.	First approach
		50	120	¼	No. 2 pos.	Succeeding approaches
No. 32 copper	No. 32 copper	120	160	1	No. 1 pos.	First approach
		120	180	1	No. 2 pos.	Succeeding approaches
No. 36 chromel	No. 36 chromel	70	100	½	—	Usually welds on second approach
		70	100	1		
0.003 in. platinum	No. 36 copper	64	90	1½	No. 1 pos.	First approach
		80	90	1½	No. 1 pos.	Succeeding approaches
No. 36 copper	No. 36 chromel	60	140	1½	No. 2 pos.	First approach
		60	140	¾	No. 2 pos.	Second approach

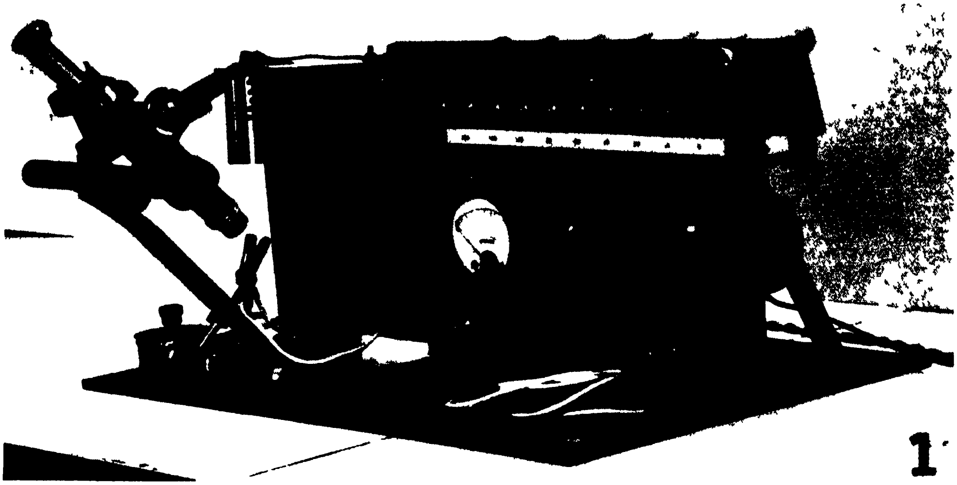

FIG. 1. *Butt-welding apparatus.*

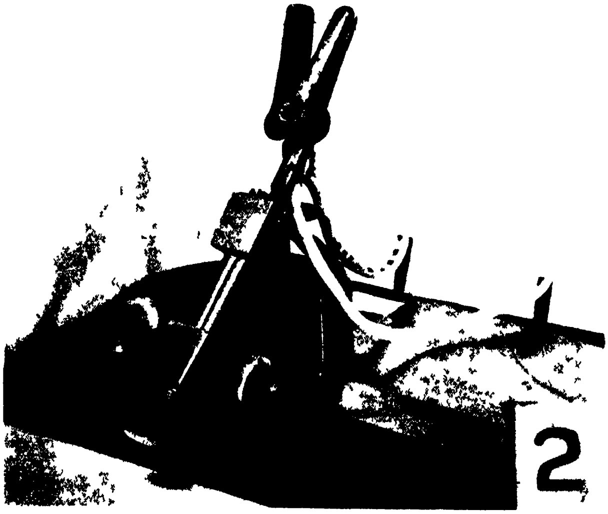

FIG. 2. *Three-way adjustable clips.*

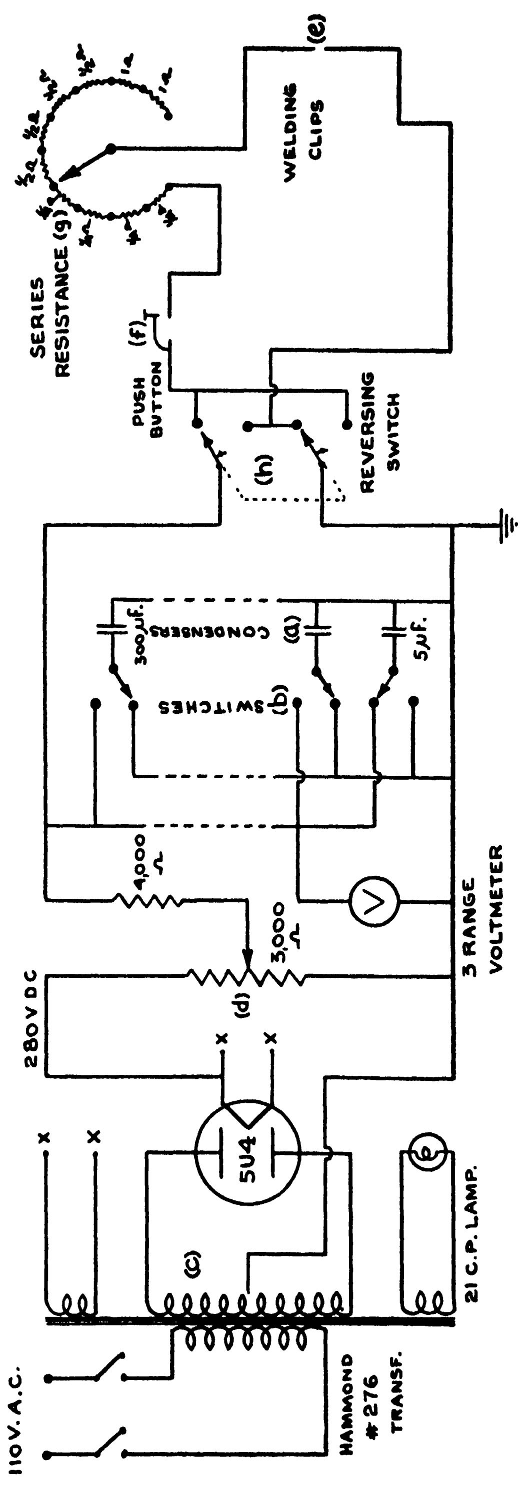

FIG. 3. *Wiring diagram.*

Properties and Applications of the Welds

Welds obtained by this method have several very desirable properties. The diameter of the welded portion is only slightly greater than that of the wires being welded and there are no sharp projections. This permits welded wires to be threaded through fine bore ceramic tubing and rubber vacuum seals. Despite their small size the welds have considerable mechanical strength and will withstand pulling and bending better than the original wires. Both the extent of the heated section and the duration of the heating are kept to a minimum, with great reduction of the amount of oxidation and annealing.

One advantage of the method is the ease and consistency with which good welds can be made. The microscope and positioning clips make aligning of the wires both convenient and accurate, and in addition the microscope offers a quick check of the weld. No particular shaping of the ends of the wires is required. Moreover, wires dissimilar in composition and size can be welded with no additional difficulty.

One of the most valuable features of the welds is the negligible thermoelectric effect in a join between two pieces of the same material. This is probably due to the small extent of the heated section and the minimized oxidation. Although temperature gradients of up to 80° C. per inch have been applied across the weld, no significant difference has ever been noted between the thermoelectric behaviour of the welded wires and unwelded wires subjected to the same conditions. Experiments have indicated that for 0.005 in. platinum or platinum – 10% rhodium, annealed before welding, the thermal effect in a weld with a 70° C. per inch gradient across it is not more than a few tenths of a microvolt, and is probably much less. Similar results have been obtained for transitions from 0.003 to 0.005 in. This neutrality of the welds makes it possible to reduce the resistance and increase the strength of lead wires by making transitions from one size to another even in regions of appreciable temperature gradient.

Although this method of welding was originally developed to make fine thermocouple junctions, the excellent characteristics of the welded joints and the ease and consistency with which they can be made have led to many other applications. To date, the apparatus has been put to the following uses:

1. Making thermocouple tips of very small dimensions.
2. Making repair joints in thermocouple leads that can be threaded through fine bore tubing and rubber vacuum seals.
3. Connecting lead wires in difficult locations by the use of portable extension leads and clips.
4. Connecting heating or thermocouple wires to low resistance lead wires, either by changing materials or by varying the diameter.
5. Repairing fine copper wire in coils without introducing discontinuities.

PLATE II

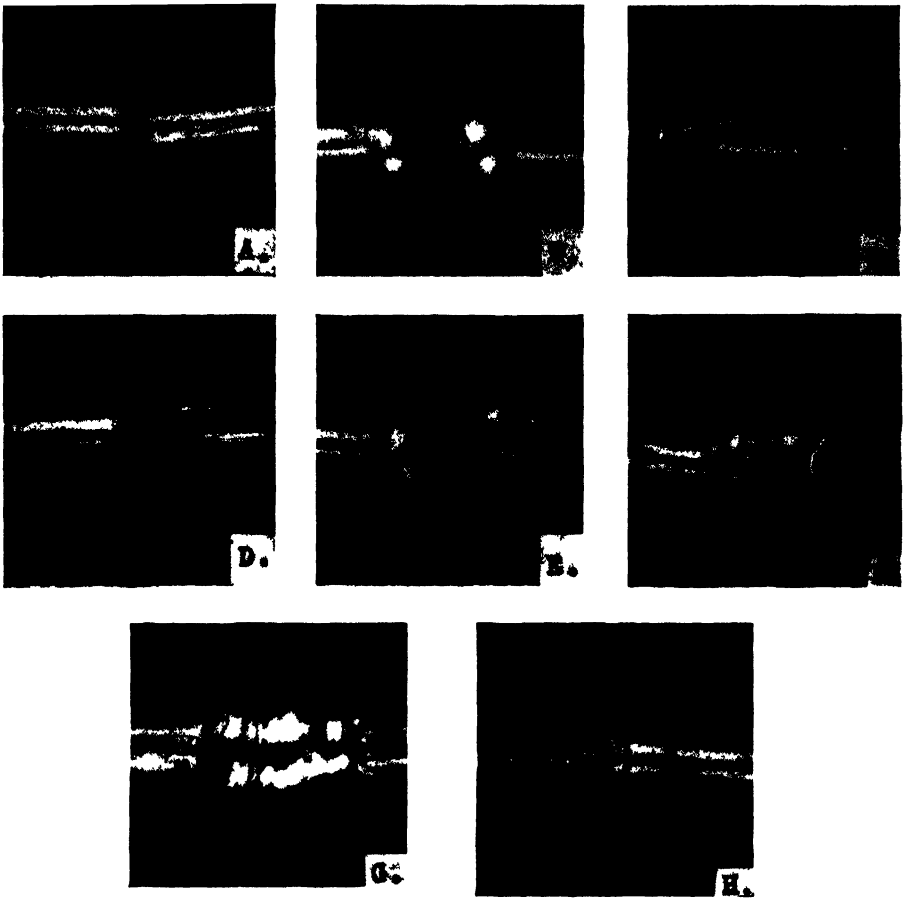

Fig. 4. *Various stages of typical welds. A, B and C. Stages in welding 0.005 in. platinum to 0.005 in. platinum. D, E and F. Stages in welding 0.005 in. platinum to No. 32 (B & S) copper. G. Completed weld between two No. 32 (B & S) copper wires. H. Completed weld between 0.003 in. platinum and 0.005 in. platinum wires.*

6. Making three-way joints for potential leads. The making of other special types of joints should be possible.
7. Making very smooth round tips for the stylus of a recorder using Teledeltus electrical recording paper. This was accomplished by using the first stage of the process with platinum wire.

Conclusion

The apparatus described offers a very useful method for welding wires of the smaller sizes, and with suitable modifications should prove applicable to wires of the larger sizes as well. The simplicity of construction and relative cheapness of the materials put it within the reach of any laboratory.

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PORTABLE GEIGER-MÜLLER COUNTERS[1]

By W. Hushley[2] and K. Feldman[2]

Abstract

Three models of portable Geiger–Müller counters which were found useful in the detection of radioactive minerals are described. The models are similar in that in each the high voltage for the Geiger–Müller counter tube is supplied by means of a multivibrator circuit and the pulse from the G–M tube is fed to a trigger circuit which actuates headphones. In one model a neon tube discharge circuit is used to give one headphone pulse for every 10 from the G–M tube and a counting rate meter is provided. Details of circuit design and application are given. The circuit of a simple amplifier that may be used with a G–M tube at the end of a long three-conductor cable is given.

General Description

Several models of portable Geiger–Müller counters which are of light weight and low power consumption were developed to meet the need for detectors of radioactive minerals suitable for field use. Three of these are described here. Their circuits, which were suggested by those published previously by others (1, 2, 3), are given in detail.

The three models *A*, *B*, and *C*, Figs. 1, 2, and 3, have a number of basic similarities. They all use self-quenching Geiger–Müller counter tubes, operated at about 1000 v. This high voltage is supplied by the same type of circuit in each case. The pulses from the G–M tube actuate trigger circuits which in turn operate the headphone and rate meter circuits.

The high voltage circuit referred to above is similar to one suggested by Huntoon (3). It consists essentially of a multivibrator with an inductive load in the plate circuit of one tube and a rectifier through which the pulses induced in the inductance charge a condenser. Negative high voltage is used, making it possible to have all the filaments near ground potential. Thus a single "A" battery may be used and the diode contained in the envelope of one of the multivibrator tubes may be used as a rectifier. The voltage to which the condenser becomes charged approaches the peak value of the pulses induced in the inductance. In each of the models described, the multivibrator has one voltage amplifier and one power amplifier type of tube with the inductance in the circuit of the latter. The power amplifier tube permits the use of low "B" battery voltages. Power requirements are reduced by using the screen grid rather than the plate of the power amplifier tube for multivibrator action. The frequency of the multivibrator is about 40 oscillations per sec. This oscillation is heard as a low hum in the headphones of Models A and B and is an indication that the high voltage section of the instrument is functioning.

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Contribution from the Division of Physics, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1532.

[2] *Physicist.*

Because of the normal variations from rated values of commercial resistors and condensers, differences in the performance may be expected in individual instruments of the same model. This is of significance chiefly in the performance of the high voltage circuit in which differences in the characteristics of the electron tubes also have considerable effect. It is often necessary to match the tubes with the remaining components of any instrument to obtain the desired range of high voltage. Differences in electronic tubes of the same type are discussed at greater length below. The 1S4 tube in Models A and C may be replaced by the 3Q4 or 3S4.

The trigger circuit consists of tubes V3 and V4 with the necessary components. The latter tube is biased beyond cut-off and a negative pulse from the G–M tube produces a single oscillation of the trigger circuit. Equalized pulses are thus available to actuate the headphones and the counting rate meter.

Model A

This model, which has headphone detection only, was designed to serve as a prospector's instrument. It may be used continuously for many hours and the batteries do not need to be replaced very frequently. The instrument weighs about 6 lb.

A circuit diagram of Model A is given in Fig. 1. Tubes V1 and V2, a 1S4 and 1S5, respectively, and their associated components comprise the high voltage section. The values of the capacities and resistances to give the desired high voltage range depend chiefly on the type of inductance L, on the particular tubes used and on the "B" battery voltage. The "B" voltage is supplied by a 67½ v. battery. The inductance used in Fig. 1 is provided by a 150 henry filter choke (Hammond No. 150, chosen for its availability and moderate weight), although, in general, audio plate reactor inductances are more efficient than filter choke inductances. The choice of condensers was

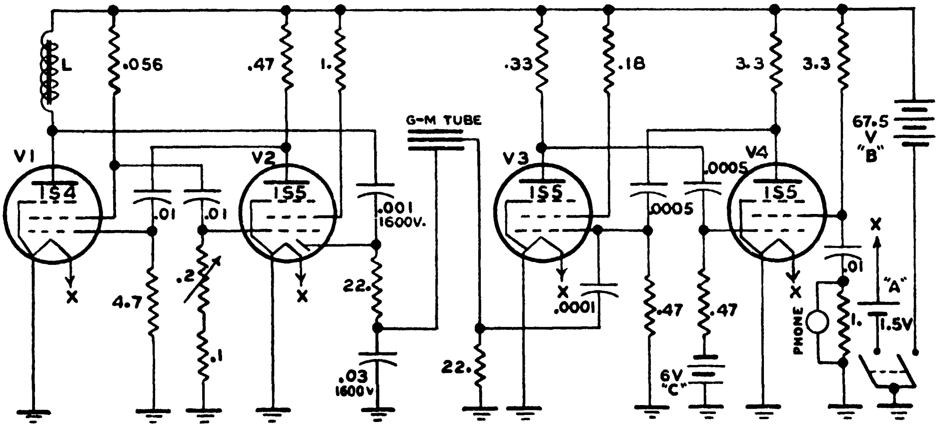

FIG. 1. *Circuit of portable Geiger–Müller counter, Model A. Resistances are given in megohms, capacities in microfarads.*

determined by their physical size as well as their capacity. The grid and plate resistor values are not critical but it is desirable to choose that combination which is least sensitive to the individual characteristics of electronic tubes and which keeps the "B" battery current near the minimum. The high voltage may be adjusted by means of the variable resistor in the control grid circuit of V2 to give a normal range from 800 to 1300 volts. Since the G–M tubes used have an operating range of about 200 v. it is not difficult to adjust the high voltage to a suitable operating value. The high voltage decreases as the "B" voltage decreases but increases as the "A" voltage decreases. These changes may be as high as 20% for the usable battery ranges. By choosing "A" and "B" batteries of appropriate capacities these effects may be made to compensate each other to some extent, and the high voltage will be almost independent of the ageing of batteries due to use.

The high impedance headphones may be operated from the screen grid or the plate of the tube V4, the pulse being louder when the phones are on the screen grid. While this instrument was designed for use where a rate meter was not considered to be advantageous, a simple rate meter (2) may be easily added by inserting a microammeter in parallel with an electrolytic capacitor in either the plate or the screen grid circuits of V4. The headphone may then be placed on the screen grid of V3 where the hum due to the high voltage ripple is louder but still not objectionable.

The "B" battery drain, which depends chiefly on the design of the high voltage circuit, is about 0.75 ma. If one uses the batteries Eveready No. 742 (1.5 v.) and No. 467 (67.5 v.) in the instrument six hours daily, the former lasts about 20 days and the latter about 40 days. Bias voltage is supplied with 'Penlite' cells.

The G–M tube used has a cathode cross-section of 2 by 6 cm. and a normal background rate of about 40 pulses per min. It was found that this pulse rate is about optimum for aural detection. An increase in the counting rate of about 50% above background is readily detectable.

Model B

The circuit of Model B, shown in Fig. 2, is similar to that of Model A. Model B, however, was designed to meet the need of a very small and lightweight instrument that would be used only intermittently.

The electronic tubes used are of the subminiature type, Raytheon 2E35 and 2E41, the former being a power amplifier tube. The tubes V1 and V2, Fig. 2, are used to develop the high voltage for the G–M tube and tubes V3 and V4 are used in the trigger circuit. Two 'Penlite' cells and two hearing-aid type batteries are used as the "A" and "B" supplies, respectively. The inductance *L* is a small 200 henry audio plate reactor (U. T. C. No. 0-13).

No provision is made for the manual control of the high voltage. The voltage obtained in any unit may be adjusted by altering the screen grid resistance of V1 or the control grid resistance of V2. With the constants given in Fig. 2, voltages of about 1000 volts may be expected. As in Model A the high voltage is very sensitive to the "A" and "B" voltages, and not all tubes prove satisfactory in the high voltage section but the unsatisfactory ones usually may be used in the trigger circuit. Each of the tube types used in the model requires a filament current of 30 ma. while the total "B" battery drain is about 0.7 ma.

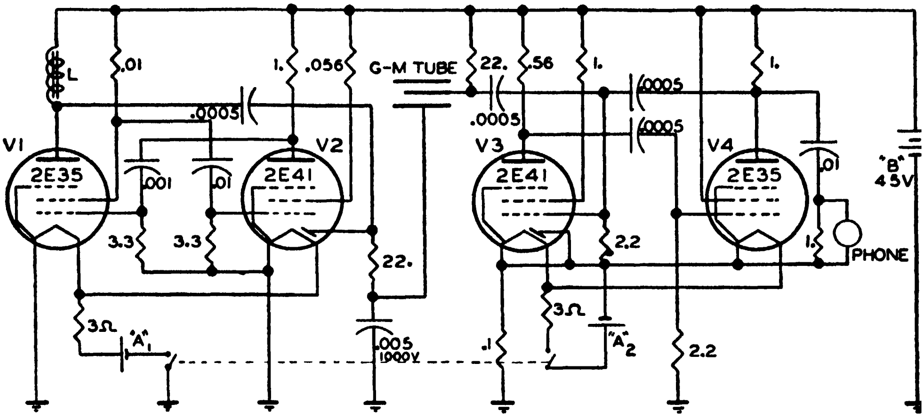

FIG. 2. *Circuit of portable G–M counter, Model B. Resistances are given in megohms, capacities in microfarads.*

As made here, the headphone and the G–M tube are both built into the chassis making the unit completely self-contained. The small G–M tube used has a normal background count of about 10 pulses per min. Using two 'Penlite' cells for the filament batteries and two Eveready No. 412 batteries for the "B" supply, the instrument may be built into a container 1 by 3 by 6 in. and will weigh approximately 1 lb. With intermittent use the batteries mentioned above will last several hours.

Model C

Model C was designed to serve as a more precise instrument for the measurement of γ-ray intensities as, for example, in surveying radioactive areas, assaying in the field, etc. It includes a counting rate meter as well as headphones. The circuit diagram is given in Fig. 3. For field work this instrument is normally used with three G–M tubes in parallel, each with a cathode 2 by 15 cm. in cross-section. The high voltage section of this model is identical with that of Model A. The trigger circuit is also somewhat similar except that tube V3 is used to operate the headphone circuit while V4 operates the counting rate meter circuit.

In the headphone circuit, the pulses from the trigger circuit cause the condenser in series with the neon tube V7 to charge through the diode of V3. When this charge becomes great enough the neon tube fires, discharging the condenser and giving a report in the phones. With the constants given,

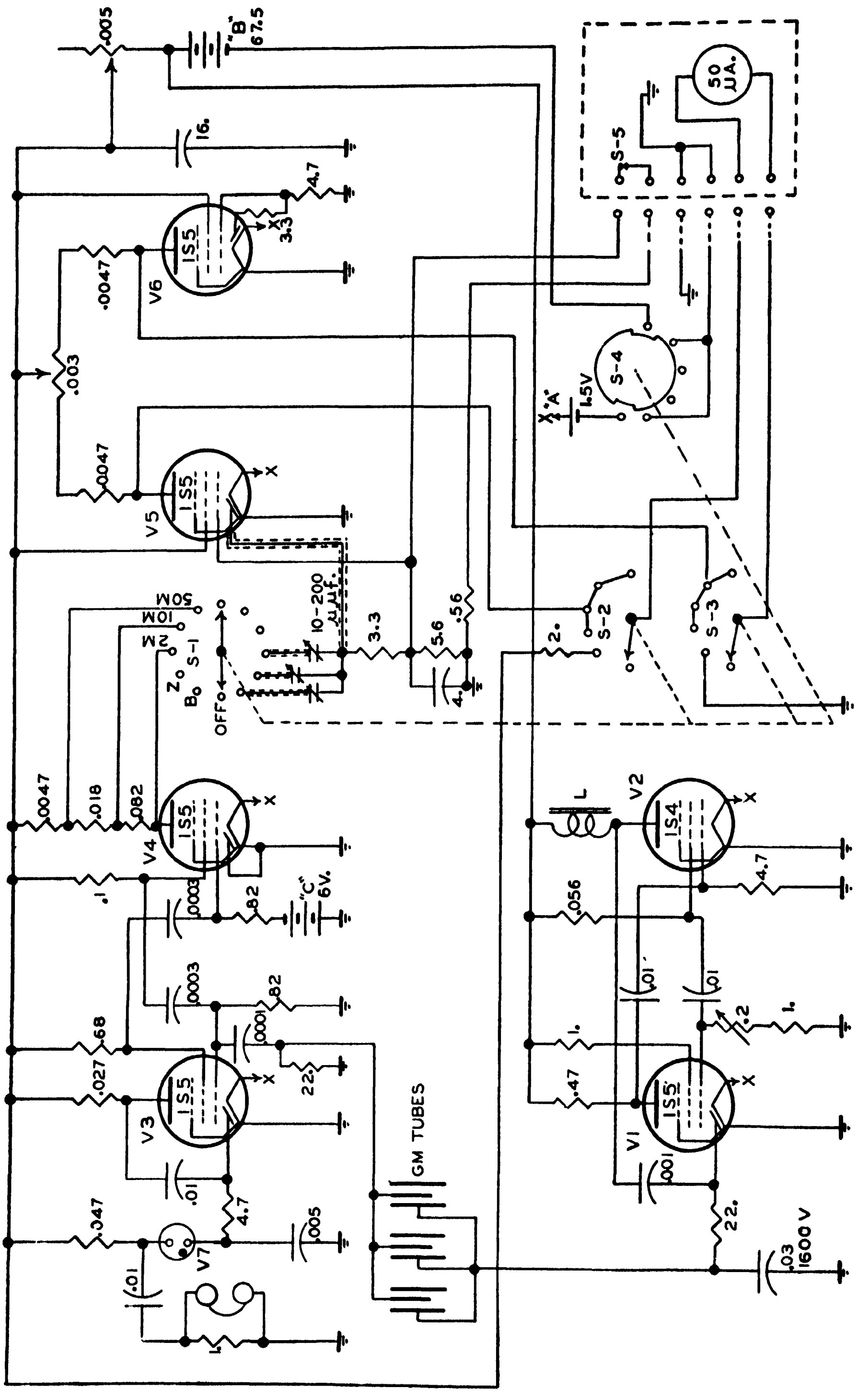

FIG. 3. *Circuit of portable Geiger–Müller counter, Model C. Resistances are given in megohms, capacities in microfarads.*

about 10 pulses from the G–M tubes give one pulse in the phones at low counting rates. This 'scaling factor' may be altered by changing the capacity of the condenser in series with the neon tube, the "B" voltage applied to the neon tube, or the characteristics of the trigger circuit. At higher counting rates the scaling factor increases and when the counting rate approaches 10,000 per min. the pulse rate of the neon tube reaches its limit. A scaling-down of the pulse rate is necessary when G–M tubes with large cross-sectional areas are used, since then a normal background count of several hundred pulses per minute may be expected and without scaling it down it would be difficult to recognize significant changes aurally. The random fluctuations in the pulse rate are also averaged out to some extent and this makes aural detection easier. This feature is of value in searching for radioactive minerals, since it allows the operator to depend predominantly on the phones for an indication of the γ-ray intensity while giving him freedom to concentrate visually on other things.

The counting rate meter has a long time constant so that reasonably steady readings are obtained even at the background counting rate. The meter reading is almost linear with pulse rate so that it may be used for quantitative comparisons. The rate meter consists of a balanced bridge circuit using two pentodes (1). By rectifying the pulses from V4 through a diode, negative charge is collected on the R-C grid circuit of V5. This causes a change in the plate current which gives a reading on the meter connected between the plates of V5 and V6. A simple analysis of the two-tube balanced circuit is given below to show that its sensitivity to the grid voltage depends on the transconductance of the first tube and the ratio of the load resistances of the two tubes. The meter reading is set to zero with the selector switch in the *Z*-position by means of the variable resistor in the plate circuit of V5 and V6. With the selector switch in the positions labelled 2M, 10M, and 50M, full scale deflection is obtained on the meter for 2000, 10,000, and 50,000 pulses per min., respectively. The final adjustment for these ranges is made by means of the variable (padder) condensers in the coupling circuit. By means of the push button switch S-5, the 4 μf. condenser may be discharged and the meter reading brought down rapidly to zero or any other desired value.

Because the operation of the rate meter, trigger, and headphone circuits is sensitive to the "B" battery voltage, this voltage is maintained at 58 v. for these circuits by means of the variable resistor in series with the "B" battery. The adjustment is made with the selector switch in the *B*-position and the voltage is read on the meter. The batteries used in this model are the same as those in Model A. The total "B." drain is approximately 3 ma.

For field work this model is fitted with the meter and the push button switch in a small meter-box at the end of a cable. A cable connector at the meter-box may be used as an On-Off switch. The meter-box is worn on a waistband while the main part of the instrument is carried in a canvas carrying case on the back of the operator. The complete unit weighs about 11 lb.

Analysis of Balanced Bridge Circuit

The following analysis shows the relation between the meter current and the applied grid voltage in the rate meter circuit described above. Referring to Fig. 4, let I_1, I_2, I_3, I_4, I_m be the current through R_1, R_2, T_1, T_2, R_m, respectively, and let the added subscript 0 indicate the current when $I_m = 0$. If k is defined by

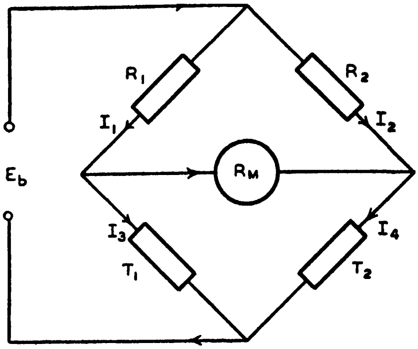

FIG. 4. *Schematic diagram of counting rate meter circuit used in Model C.*

$$k = \frac{R_1}{R_2} = \frac{I_{20}}{I_{10}} = \frac{I_{40}}{I_{30}}\,, \tag{1}$$

then application of Kirchoff's laws shows that

$$I_m = \frac{I_4 - kI_3}{k + 1 + R_m/R_2}\,. \tag{2}$$

In the rate meter circuit, R_m is the meter resistance and if $R_2 \gg R_m$ then approximately

$$I_m = (I_4 - kI_3)/(k + 1)\,. \tag{3}$$

If I_3 and I_4 are written $I_{30} + \triangle I_3$ and $I_{40} + \triangle I_4$ then Equation (3) becomes

$$I_m = (\triangle I_4 - k \triangle I_3)/(k + 1)\,. \tag{4}$$

Let the two components T_1 and T_2 be vacuum tubes and let the grid potential of T_1 be changed by $\triangle E_c$ while T_2 is left unchanged. Then $\triangle I_4 = 0$ and $\triangle I_3 = G_m \triangle E_c$ where G_m is the transconductance of T_1 and is assumed constant. Equation (4) then becomes

$$I_m = -\,G_m \triangle E_c k/(k + 1)\,. \tag{5}$$

For a balanced circuit with equivalent components this simplifies to

$$I_m = -\,\tfrac{1}{2}\,G_m \triangle E_c\,.$$

Thus the meter current I_m is a linear function of the grid voltage E_c and is independent of the absolute values of the load resistances. However, the latter should be high compared to the meter resistance to maintain sensitivity.

The linearity of the rate meter depends on the collecting circuit which determines E_c and on the transconductance of V_6 remaining constant.

If the tube T_2 is replaced by a resistance R_4 then

$$\triangle I_4 = I_m R_2/(R_2 + R_4) \ ,$$

and

$$I_m = - G_m \triangle E_c \frac{k}{k+1}\left[\frac{1}{1 - R_2/(R_2 + R_4)(k+1)}\right] . \qquad (6)$$

From Equation (6) it may be seen that the use of a divided resistance for half of the balanced circuit results in increased sensitivity. Replacing the vacuum tube by a resistance also reduces the filament current required, but it has the disadvantages that the zero-set of the meter is very sensitive to the "B" voltage, and the time lag in the filament emission when the instrument is turned on may cause a surge of current through the meter.

Electronic Tubes for the High Voltage Circuit

Tests were made on about two hundred 1S4 and 1S5 electronic tubes to determine their suitability for use in the high voltage circuits described in this paper.

The 1S4 tubes were from two lots made by different manufacturers and were tested in a given circuit of the type described for Models A and C, with a given 1S5 tube. Under the fixed conditions 25% of one lot and 35% of the other gave a maximum high voltage of less than 1000 v. while 60% of the first lot and 45% of the second gave above 1100 v. There seemed to be little correlation between the maximum high voltage and the range over which it could be varied by means of the high voltage control.

The 1S5 tubes were from three lots made by different manufacturers. In this test the tubes were classified as good, fair, and poor, according to their general performance, such as maximum high voltage obtained and the rate of leakage of charge after the instrument is turned off. The results obtained are given in Table I.

TABLE I

CLASSIFICATION OF 1S5 TUBES IN HIGH VOLTAGE CIRCUIT

Classification	Lot 1	Lot 2	Lot 3
Good, %	10	50	85
Fair, %	15	25	10
Poor, %	75	25	5

This table points out a serious disadvantage in using this type of high voltage supply in that satisfactory performance depends a great deal on the particular lot of electronic tubes being used. In one test the diodes of the 1S5 tubes were used independently of the pentodes. The test showed individual variations in high voltage of as much as 150 v. for diodes that showed no other irregularities such as excessive leakage or breakdown. On the average, potentials in excess of 1500 v. are required to cause breakdown in the diodes. The performance of the 1S5 tubes in the circuit does not depend, however, on the diode alone.

The results given are typical of other tube types such as 3A8GT, 1D8GT, and 2E41. When a group of satisfactory tubes are classified in order of merit as tested in a given high voltage unit, this order is not necessarily the same in another unit. However, poor tubes are usually not good in any high voltage unit though they may generally be used in the trigger sections of the instruments.

Amplifier for Geiger-Müller Counter Probe

It is sometimes necessary to use a G–M counter tube in a probe at the end of a long cable. The capacity of the cable reduces the amplitude of the voltage pulse from the G–M tube and it is necessary to use an amplifier in the probe end of the instrument. Fig. 5 shows a circuit that may be used with a three-conductor cable. The probe contains only the G–M tube, an electronic tube, and two resistors. The current drawn from the high voltage supply is about 1 μa. Such an amplifier has been used at the end of 1000 ft. of three-conductor 'cab-tire' cable in a portable counter designed for surveying diamond-drill holes.

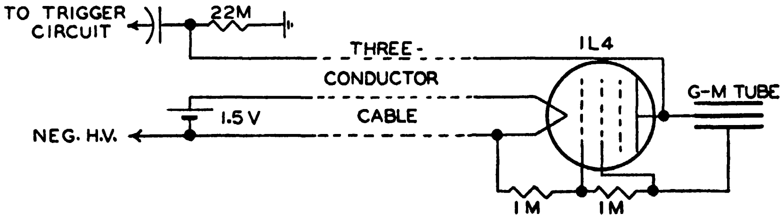

FIG. 5. *Circuit of an amplifier for a Geiger–Muller counter probe.*

Effect of Temperature on Portable Counters

Low temperature will affect the operation of the counters described here by condensing the organic vapour in the self-quenching G–M tubes and by reducing the efficiency of the batteries. The first effect can be eliminated by using an organic compound such as ether, which does not condense at the temperatures at which counters are normally used. The reduced efficiency of the "A" battery causes an increase in the high voltage which is compensated by the effect of the lower "B" battery voltage. The net result is usually some increase in the G–M tube voltage. If the change in temperature is accompanied by the condensation of moisture in the instrument the high voltage will be reduced considerably. Most of the instruments made here were not used in areas of high relative humidity and effects of humidity were not considered in their design.

Acknowledgments

The authors wish to acknowledge the assistance received from other members of this laboratory in the design and construction of portable Geiger-Müller counters.

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A LABORATORY SHAKER[1]

By W. Harold White[2]

Abstract

A laboratory shaker is described that employs an eccentricless drive. The machine has sufficient flexibility in design to permit variable temperature and speed control. It has a capacity of two dozen 500-ml. flasks.

Introduction

Several years ago, a survey of existing laboratory shaking apparatus showed that an efficient machine of large capacity, suitable for certain types of food analysis, was commercially unobtainable. Special requirements, notably sufficient flexibility in design to permit variable temperature and speed control, prompted the designing of a machine embodying temperature maintenance at approximately 100° C., speed variation by means of cone pulleys, capacity for two dozen 500-ml. flasks, and a drive that does not depend upon eccentric motion. The present article has been prepared in response to requests for details of construction.

Details of Construction

The apparatus shown in Fig. 1 did not make use of the usual eccentric drive, since it was found that eccentric motion produced too abrupt a movement, particularly at high speeds. This obstacle was overcome by using the Eureka–Buhler 'eccentricless' drive,* consisting of two counterweighted steel wheels enclosed in drums, shown at *B* in Fig. 1, supported by a base-plate, *L*, and geared to rotate in opposite directions. The counterweights were so arranged that when they were in the vertical plane the centrifugal forces exerted by their rotation were equal and opposite, whereas when they were in the horizontal plane the forces were additive and produced a shaking motion.

Length of body travel is dependent upon the speed used and the weighting of the steel wheels at the factory; a travel of $\frac{1}{2}$ in. at the lowest speed was found to be most suitable for normal needs. As the speed of the shaker depends upon the speed of rotation of the steel wheels, variation may be obtained by changing the ratios on the cone pulleys at *C* and *K*, side view at *D*. Power was supplied by a 1/6 h-p. electric motor, *C*.

The apparatus may be mounted upon castors for mobility, as shown, or permanently established on wooden blocks.

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Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa. Issued as Paper No. 191 of the Canadian Committee on Food Preservation and as N.R.C. No. 1527.

[2] *Formerly Biochemist, Food Investigations; at present, Research Chemist, Imperial Oil Co. Ltd., Sarnia, Ont.*

* *Obtained from S. Howes Co., Inc., Silver Creek, N.Y.*

The supporting framework was constructed from 1½ in. angle iron in the following dimensions: length, 3 ft.; width, 1 ft. 6 in.; height, 2 ft. 4 in.

The body of the shaker was constructed of 1-in. lumber, to form an open-top box 3 ft. 3 in. by 1 ft. 4 in. by 10½ in., outside dimensions. A copper steam chest, 1 in. in height and containing copper steam coils, was fitted into the bottom of the box, covered with a ¼ in. layer of felt to avoid damaging glassware, and overlaid with 1¼ in. insulation board, with holes of proper diameter to hold flasks of the desired size. These details are indicated in the cut-away section, *I*, in which the top layer represents the insulation board.

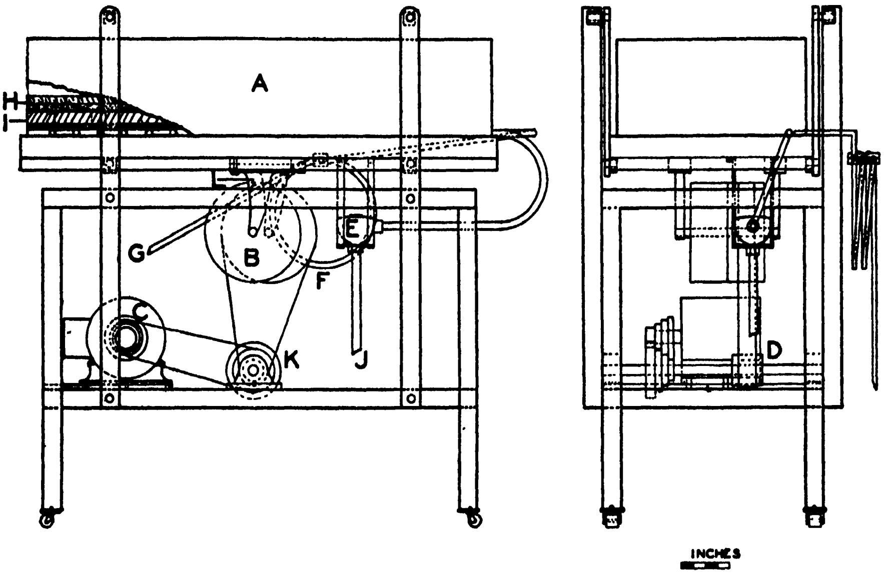

FIG. 1. *Side and end views of a laboratory shaking apparatus.*

A 7/16 in. plywood board cover, fitted with ½ in. felt insulation, is shown in section at *H*, resting on section *I*. This cover, with holes through which the flask-necks protrude, holds the flasks firmly in place.

The body of the shaker was mounted on four sets of bearings, two sets being shown in the end view in Fig. 1. This indicates a ½ in. flat brass bearing at the top of the supporting arm; at the bottom of the arm is a ½ in. rod, connected as an axle to the corresponding opposite arm.

Steam was introduced at *G*, representing the copper tubing inlet, passed through a shock-absorbing coil, *F*, which absorbed the motion produced when the shaker was in use, and thence to the metal steam chest. Returning steam was passed through a steam-trap, *E*, and any condensed water drained off through the outlet, *J*.

Thermostatic control may be installed for temperatures below 100° C., by circulating water from a temperature controlled reservoir in place of steam.

A LARGE CYLINDER AND TAPER COMPARATOR FOR GAUGE MEASUREMENT[1]

By R. H. Field[2]

Abstract

The measurement of the diameters of cylinders and cones is an important feature in gauge manufacture and inspection. High accuracy is essential in this work, as the objects measured may be employed as limit gauges for use in the inspection of other precision gauges to which direct means of measurement cannot be applied. A comparator for accommodating cylinders or cones with maximum diameters of 12 in. and lengths up to 48 in. was designed and constructed during Great War II at the National Research Laboratories, Ottawa, and used throughout the war. In preparing the design special consideration was given to ease of construction and no ultra precision grinding or difficult fits were involved.

Introduction

It is the usual practice to measure the diameters of cylinders or cones, in the metrological laboratory, with the object standing vertically (the small diameter downward in the case of cones) while micrometer measurements are made across the outside of two small horizontal cylinders contacting the object and resting on the tops of vertical end-bars (1, page 89). While this operation can be carried out with the aid of a hand-held micrometer caliper, considerable skill is necessary on the part of the operator, who, moreover, has to work under uncomfortable conditions. Even then, a precision of measurement better than 0.001 in. is difficult to attain. To make the operation easier to perform and to increase the precision to conform to modern requirements in engineering practice, a range of comparators was designed by the National Physical Laboratory, England, to be used exclusively for measuring the diameters of cylindrical and conical objects. These instruments permitted readings to be estimated to 0.00001 in. or 0.00002 in. The N.P.L. kindly supplied working drawings of these instruments to the National Research Council, and two of the smaller (bench type) comparators were constructed to these drawings, with slight modifications. For the large size the N.P.L. scheme entails somewhat difficult shop work during construction, and it was felt that an alternative design would not only make possible improvements in the operation, but would present fewer difficulties in the shop. Therefore, when war needs became urgent, the comparator here described was designed by the author, and constructed in the Instrument and Model Shop of the National Research Laboratories.

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[2] *Metrologist, Head of Metrology Section.*

Description

An illustration of the complete instrument is reproduced in Fig. 1. The over-all height is 72 in., the maximum diameter which can be accommodated is 12 in. and the anvils can be set at any height in the range of 1.5 in. to 48 in. above the top of the base. In use the comparator is supported on a heavily built stool 18 in. high, so that the lower ends of the objects being measured are accessible.

Fig. 2 shows the lower portion of the comparator and some details not visible in Fig. 1, while Fig. 3 illustrates the micrometer carriage and its support, which can be set and used over a range of heights. In the view the parts in question are shown dismounted from the comparator and from one another.

Base

The complete assembly is carried by a cast-iron base-plate having a boss at the rear bored to receive the turned lower end of the column supporting the measuring unit, and three flat bosses fitted with the usual vee, cone, and plane shoes (of hardened steel) for locating the foot-screws of the adjustable table for supporting the object. Two other bosses are fitted with 'safety' pegs in case the table should be accidentally tipped.

The table is a heavily ribbed iron casting, planed at the top. It was intended in the original design to fit a hard steel plate, checkered and lapped on its upper face and held to the iron table by clamps located in vee grooves in the edges of the plate. This plate was not made, and the lapped loose steel plate, seen in Figs. 1 and 2, was found quite satisfactory. The bronze foot-screws, tapped into inserted nuts beneath the table, permit the upper reference surface of the steel plate to be accurately levelled for measuring operations, without making any exacting demands on the machinist at the time of construction.

Column

The column forming a support and guide for the diameter-measuring unit is made from a piece of square bright steel, 1.75 in. diam. with the corners planed to give tracks 0.5 in. wide for the rollers on the vertical sleeve described below.

Sleeve

The measuring unit is carried by the sleeve seen best in Figs. 2 and 3. This sleeve comprises a hollow casting, with planed lugs for two horizontal cold-rolled steel rails, having their sides ground, and it has two crown castings located by spigots and attached by screws at its upper and lower ends. Each crown piece serves to hold four ball bearings, 30 mm. O.D., which contact the tracks formed on the corners of the column. The axles for the bearings are eccentric, permitting close fitting and adjustment of the sleeve without difficulty. By this means the sleeve is allowed to traverse up and down the column quite easily, with no tendency to bind, but is yet free from 'shake'. Furthermore the eccentric axles permit the supporting rails of the micrometer carriage to be made truly horizontal.

A lug on the upper crown casting has a bronze nut inserted, and this engages the vertical setting screw seen in Fig. 2. The sliding casting on which the screw is located in a journal is a free fit on the column, with a brass shoe bearing against one of its sides when the clamping screw is tightened. Thus the micrometer anvils can be set and held at any desired height above the base. A cable is fastened to the sleeve, and, passing over a pulley on a bracket at the top of the column, is attached to a counterweight in the vertical tube seen to the rear of the column in Fig. 1. A light finger touch on the setting screw is sufficient to raise or lower the whole assembly.

To protect the bearings and rails from dirt, a light metal cover having a hinged door at the front, is located on the two posts seen threaded into the upper rail in Figs. 2 and 3.

Micrometer Carriage

The micrometer head and the indicator are mounted on a carriage having a free horizontal movement of about 1 in. To provide this movement without undue friction, which would falsify the indicator settings, or looseness in fit, which would impair accuracy, the carriage is carried and located by means of ball bearings on the two rails attached to the sleeve. The bearings are mounted on two built-up brackets connected together by a bar at the top, and at the bottom by a slide. This slide, which was part of a discarded instrument used for other purposes, forms a horizontal bed for the brackets carrying the micrometer and the indicator.

Two of the ball bearings carry the weight of the movable carriage, and engage with the upper surface of the lower rail. Two others with vertical axes bear against the front face of the rail, to take the reaction from the weight moment of the overhung carriage. Finally, a pair of bearings with vertical axes at the top of each built-up bracket engages with the vertical sides of the upper rail, leaving a sole degree of freedom for the carriage in the direction of the micrometer-screw axis. As in the case of the sleeve, the ball bearings are all mounted eccentrically to permit easy adjustment and the elimination of lost motion.

The free movement of the carriage is limited by rubber buffers fitted into housings screwed to the ends of the upper rail on the sleeve.

Micrometer System

The micrometer and indicator are each inserted in holes formed in ribbed offset brackets, with split lugs for clamping. These holes were lapped in line at the same time while the brackets were mounted on the bed. As can be seen in Fig. 3, the tee slot in the bed permits the brackets to be clamped rigidly at any desired spacing, for actual measuring purposes.

PLATE I

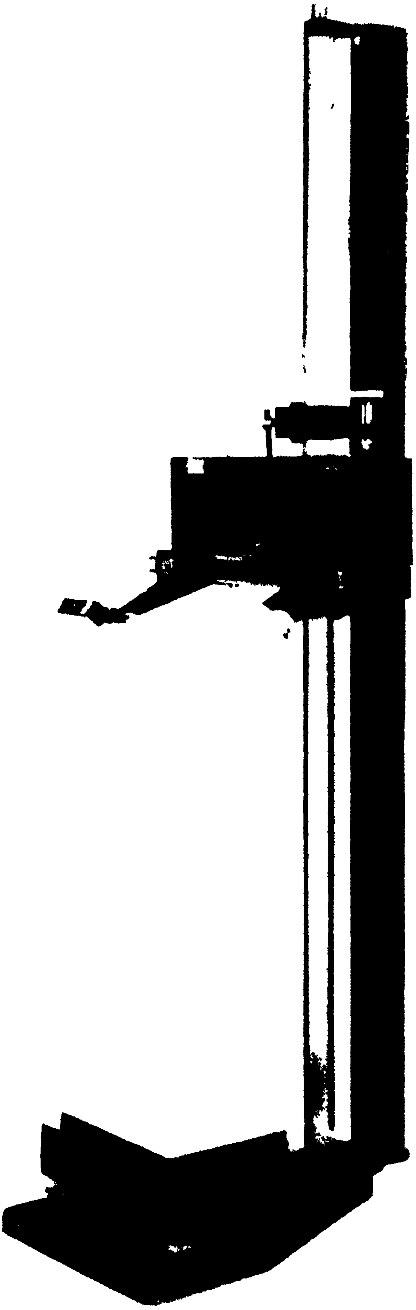

FIG. 1. *The comparator designed and constructed in the National Research Laboratories for measuring large taper and cylinder gauges.*

PLATE III

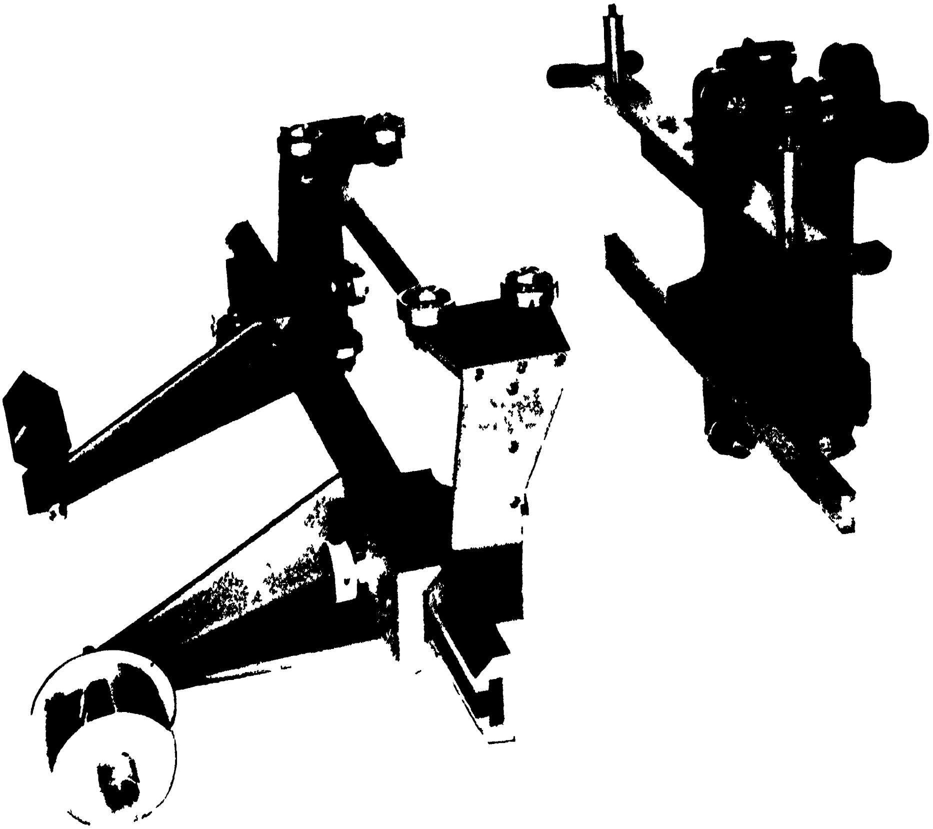

FIG. 3 *Left* *The movable carriage dismounted to reveal more details. The ball bearings permit the carriage to be located closely on its two supporting rails and yet to move freely in the axial direction of the micrometer screw.*

Right *The support for the rails holding the carriage. This support travels freely up and down the main vertical guide of the comparator, being located by two sets of four ball bearings, mounted on eccentric arbors to permit easy adjustment and lining up.*

For the micrometer a selected and tested commercial micrometer head having a range of 1 in. was fitted with a duralumin drum of 2.5 in. diam. graduated to read directly to 0.0001 in., while a N.P.L. type of indicator, needing a pressure of 0.5 lb. to bring the hand opposite the fiducial mark, was used.

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AN IMPROVED INTERFEROMETER FOR DETERMINING PARALLELISM ERRORS IN LONG END-GAUGES[1]

By L. Graham Turnbull[2]

Abstract

This paper describes an interferometer designed for the determination of the parallelism of the working faces of end-gauges up to 24 in. in length. An instrument for this purpose, but which required somewhat highly specialized technique in the course of its construction, had been previously designed by the National Physical Laboratory. Using optical principles the same as those of the British instrument, another of an entirely new mechanical design has been constructed by the National Research Laboratories, Ottawa. This new interferometer incorporates kinematic principles and a number of interesting features to permit easy adjustment and operation to the very fine limits necessary. By the addition of a sensitive level vial to this instrument, the difference in length of nominally equal end-gauges can be determined to an accuracy of 1 or 2 $\times 10^{-6}$ in.

Introduction

In establishing the length of an end-gauge, complete knowledge of the interparallelism of the gauging faces is of the greatest importance where high precision is required. This is especially true when several gauges are to be wrung together, in which case the derived length of the combination is not the sum of the lengths of the individual gauges, unless the parallelism errors be taken into consideration.

Previous to the outbreak of World War II, the parallelism errors of end-gauges of 3 in. or less in length were determined (absolutely) in the Metrology Section of the National Research Laboratories, Ottawa, by rather laborious interferometric methods; longer gauges were measured by making a large number of comparisons with nominally equal combinations of shorter gauges of known parallelism.

In the National Physical Laboratory, there already existed an instrument known as a Flatness Tester (1), which could be used in the measurement of long end-gauges. In 1940, as the war progressed, the number of gauges of the Johansson type submitted to the National Research Laboratories, Ottawa, rapidly increased, and it was soon realized that (especially in the case of the longer end-gauges) an instrument that could do the same work as the N.P.L. instrument would have to be devised in order to attain more precision and speed in the measurement. The interferometer described in this paper was therefore designed by members of the scientific staff of the N.R.L. to meet this contingency. The basic principle of this apparatus essentially follows that of the N.P.L. flatness tester, but several novel features have been incorporated, and an entirely different mechanical design has been adopted.

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Contribution from the Division of Physics and Electrical Engineering, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1534.

[2] *Metrologist.*

Principle

The theory of the interference of light is given in elementary textbooks on physics and optics. It is sufficient to state that when a partially reflecting, optically flat surface (e.g., of quartz or glass) is placed above a second optically flat reflecting surface so as to be nearly parallel to, and almost touching it, interference fringes may be formed. When viewed through the upper plate, these may be seen as a series of parallel, equispaced bands apparently located on the lower surface.

In the parallelism interferometer these interference effects are utilized in the measurement of parallelism errors. Here, an optically flat quartz disk is arranged above the upper optically flat gauging face of an end-gauge in the manner just described. A parallel beam of monochromatic light, passing through a semitransparent mirror which is inclined to the path of the beam, falls normally on to the gauge. If the eye be correctly placed with respect to the mirror so as to receive the reflected rays from the end-gauge, interference fringes may be seen against the background of the gauging face. If then, the gauge be rotated with respect to the flat, through 180° in the plane of its lower gauging face, the spacing of the fringes will alter, unless the working faces of the gauge be co-parallel. The difference in fringe spacing is a measure of the change in the acute angle contained by the plane of the optical flat and the plane of the upper surface of the gauge, and is, hence, a measure of the parallelism error between the gauging faces themselves.

Fig. 1 is a schematic diagram of the optical system of the actual interferometer. In this figure, 1 represents the light source, a mercury arc, rendered reasonably monochromatic by means of a suitable filter, 2. A lens, 3, is used to obtain a sensibly parallel beam of light Parts 1, 2, and 3 are constructed as a unit, placed outside a small glass window in one of the walls of the temperature-controlled room, in which the parallelism interferometer is located This separation was made in order to minimize any heating effect that the arc might have on the interferometer, and to exclude from the room the objectionable odours that emanate when the arc is in operation. An adjustable plane mirror, 4, situated vertically above the interferometer, directs the beam of light on to a lens, 5. This lens brings the rays to a focus on a small circular aperture, 6 (approximately 1 mm. in diameter), located centrally in a thin brass diaphragm, 7, which is adjustable with respect to the lens, 5. The last two components constitute a unit that can be adjusted in such a manner that the aperture can be placed at the focus of a lens, 8, which again collimates the beam of light. Interposed between the aperture and lens is a semisilvered plane glass mirror, 9 (which is adjustable), making an angle of approximately 45° to the optical axis. From 8, the rays pass through a quartz disk, 10, the lower face (known as the 'proof-plane') of which is optically flat to about 0 000001 in. Interference fringes are formed between this face and the upper surface of an end-gauge wrung on the working surface of another quartz 'flat', 11, finished to the same degree of flatness as the first. The quartz 'flat', 11, in the case of the Canadian instrument, is set in the upper end of a vertical cylindrical barrel, described in more detail below, which can be made to rotate in such a manner that the working face of 11 will turn in its own plane or in planes parallel to it. The interference pattern may be viewed through a peep hole, 12, which receives the pattern from the semireflecting face of the glass mirror, 9. A mount, 13, fabricated mainly of brass sheet, contains most of the elements 5 to 12, inclusive.

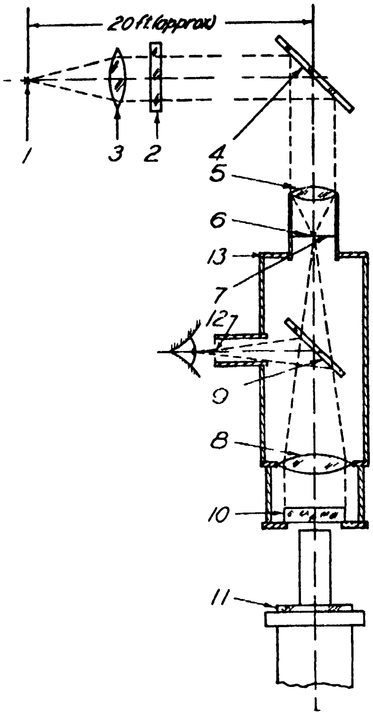

FIG. 1. *Schematic drawing of the optical system of the parallelism interferometer.*

Distinctive Features of the British and Canadian Interferometers

In the British interferometer the turntable is of steel in the form of a disk, with its working faces lapped very flat and accurately parallel. The lower face rests on another equally flat surface formed on the bed of the instrument, so that the upper working face (to which the end-gauge can be wrung) can rotate in its own plane, with very little error. The turntable is constructed of a special high-carbon chrome steel, and is heat treated by the steel maker before lapping. Special technique (i.e., spot grinding) is required to obtain the high degree of precision in flatness and parallelism. The turntable in the Canadian interferometer, on the other hand, requires for its fabrication only such facilities as are available in an ordinary machine shop.

As has been stated above, the turntable of the N.R.L. interferometer consists of a vertical barrel, in the upper end of which is set a quartz base-plate. The working face of this plate can be made accurately perpendicular to the axis of rotation of the turntable by easy adjustments. In addition, by means of a mirror placed suitably beneath it, the degree of wringing of an end-gauge to the working face can be readily observed and controlled—a feature that has been found to speed up considerably the time involved in the measurements.

Furthermore, in the Canadian instrument the interferometer mount is movable on rollers and is counterweighted so that it can be quickly set into any desired position on a long vertical rod. Moreover, the proof-plane 10 is carried on a platform integral with the interferometer mount.

In the N.P.L. interferometer, the adjustment of fringe spacing and configuration is obtained by tilting the mount which carries the proof-plane, while in the N.R.L. apparatus, coarse adjustment is obtained by tilting the proof-plane itself, and fine adjustment by altering the inclination of the supporting rod.

Design of the N.R.L. Parallelism Interferometer

The design of the instrument will be considered in two parts: (I) that concerning the optical system, the principle of which has been described above in some detail, and (II) that which deals with the means for obtaining the condition that the working face of 11 will rotate in its own plane or in planes parallel to it.

(I) *Optical System*

Fig. 2 is a photograph of the parallelism interferometer, the over-all dimension from top to bottom of which is approximately 6 ft. Seen at the top of the photograph, is the mirror 4, adjustable on a brass rod which is screwed to a baseboard, attached to the wall. Vertically below the mirror is the mount 13.

This mount, a close-up view of which is shown in Fig. 3, is capable of travel up and down, and to a limited extent, around, the vertical brass tubular rod (seen at the immediate left of the mount) which is suspended by means of gimbals at its upper end. In the lower or free end of the vertical tube is inserted a steel plug, which is held by spring closure against two mutually perpendicular tangent screws in a horizontal plane. By means of these screws, final (fine) adjustment of the interference fringe spacing and configuration may be accomplished by the slight change in inclination imparted to the whole mount, and therefore to the proof-plane. The location of the screws is shown in Fig. 2.

A counterweight, encased in a vertical sheet-metal cylinder, at the extreme left of Fig. 2, is attached to one end of a phosphor-bronze wire which passes over two pulleys; the other end of the wire is fastened to the mount. By this means, the latter can be moved readily up and down and set into convenient positions on the supporting tube, no clamp being necessary.

Referring to Fig. 3, the upper end of the mount maintains closed contact with the supporting rod by means of three cylindrical rollers, equally spaced about the rod axis. The remaining constraints are obtained by means of a pair of conical rollers at the lower end, which are held in contact with the vertical rod by gravity. Each roller, or pair of rollers is fitted on an eccentric axle to permit ready adjustment. Thus, free movement without backlash is achieved, and the effect of inequalities arising from wear, lack of straightness, etc., in the tube is eliminated.

The unit containing the elements 5 and 7 (i.e., condensing lens and diaphragm) can be seen at the top of the photograph. It is a brass tube, the lower end of which is threaded, for the purpose of adjustment, into the top plate of the mount. Behind the eye-diaphragm (near the centre of the photograph) can be seen the knurled heads of four screws used in adjusting and clamping the mirror 9.

Directly below the screws, at the bottom of the mount, can also be seen the edge of the cell containing the collimating lens 8. Beneath this again is a brass ring, in which the quartz flat 10 is supported. For the purpose of coarse adjustment (of the proof-plane with respect to the upper face of the end-gauge) this ring may be tilted by means of the arrangement shown. Here, three oversize holes in the ring receive, respectively, three brass studs which are threaded into the lower base-plate of the mount. The free, or lower, ends of the studs are also threaded for about 1 in. of their length, and on each, a nut is screwed to the limit of its run. Enclosing the threaded portion of the free end of each stud is a helical spring, one end of which is held against the nut, while the other end butts against the ring. Another nut, with which the actual adjustment is made, forces the ring against the spring.

A metal stop in the form of a ring, which can be clamped at any desired position on the vertical rod, is provided to prevent overrunning of the mount. Also provided is a series of thin Masonite covers, one of which is shown around the end-gauge in Fig. 2. These not only serve to insulate the gauge from convection currents and radiation, but also to protect it from accidents.

(II) *Turntable*

Fig. 4 is a cross-sectional drawing of the turntable of the N.R L. parallelism interferometer. In this figure, 14 is a massive cast-iron bracket which supports the entire lower assembly and which is rigidly bolted to the concrete wall. Into the base of this casting is fitted vertically, a truncated conical steel spindle, 15, about 24 in in length. The latter has a long fit in the base of the bracket, and is pulled firmly against a shoulder by means of a nut. At the upper and lower ends, respectively, of the vertical spindle, and fitted concentrically to it, are cylindrical bushings, 16 and 17, each with its outer face hardened, ground, and lapped. Concentric with 16 and 17, and with their mating faces lapped to fit them, is a corresponding pair of bushings, 18 and 19. These latter are fitted into a cylindrical steel pipe, 20, in the upper end of which is attached a steel plate, 21, about ½ in. thick. This plate serves as a housing for a tempered steel stalk, 22, concentric with it and which is held against a shoulder by means of a hollow screw, 23. The lower face of this stalk, which is about 1½ in. long, is hardened, ground, and lapped flat

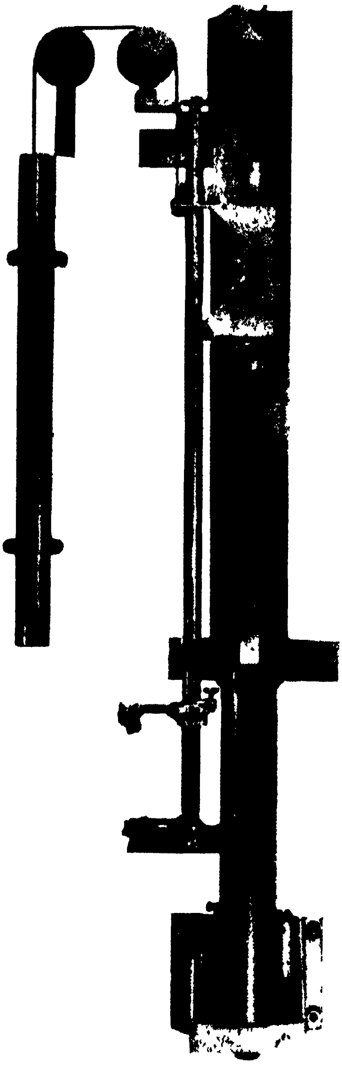

FIG. 2.

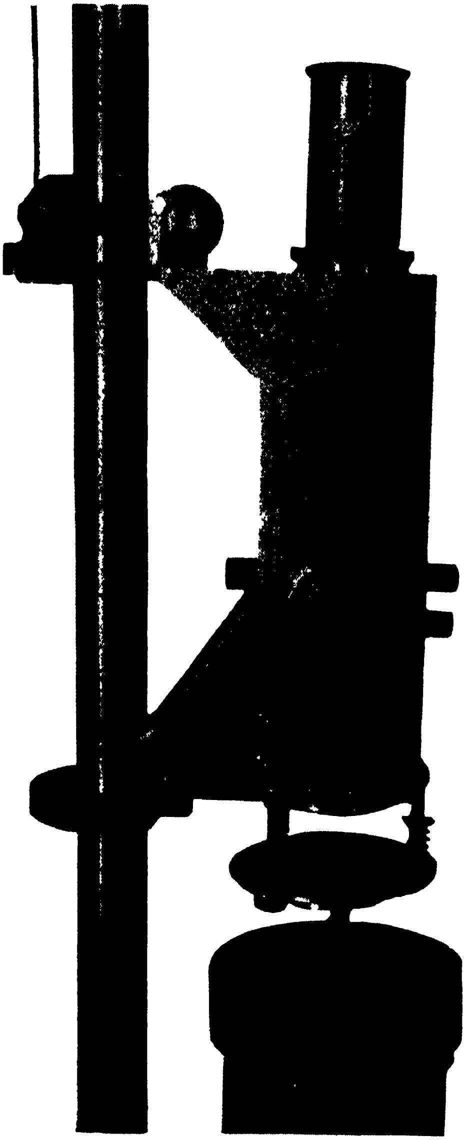

FIG. 3.

FIG. 2. *Photograph of the interferometer showing a 20 in. end-gauge in position for measurement. Below the gauge and to the left of it are the level vial and attachments used when the instrument is to be employed as a level comparator.*

FIG. 3. *Close-up view of the mount with a short end-gauge in position. The reflection of the wrung surface of the gauge can be seen in the inclined mirror beneath it.*

and perpendicular to its geometric axis. This face which is approximately 3/16 in. in diameter, rests on a hard steel ball, 24, peened into a hole in an auxiliary steel end-piece which is screwed coaxially on to the central spindle, 15. The upper end of the stalk is centrally located in a cast-iron plate, 25. In the upper face of 25 are symmetrically fitted three steel pins, 26, on which

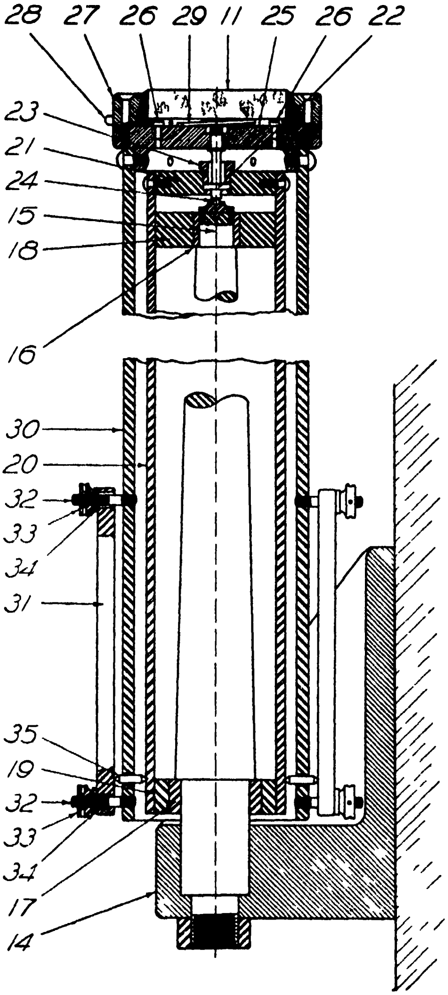

FIG 4 *Cross-sectional drawing of the turntable*

rests the quartz flat, 11. The flat is held in position against these pins by means of plaster of Paris, which fills the space between the cylindrical surface of the quartz flat and a cast-iron annulus, 27, attached by means of screws to 25. Leading into the space beneath the flat is a short brass tube, 28, to permit the use of an air pump for the removal of moisture. In this space is fixed a circular mirror, 29 (seen immediately below the quartz flat in Figs. 3 and 9), which is approximately 2 in. in diameter, and which has its plane inclined about 5° to the plane of the working face of the optical flat, in order to avoid undesirable reflections. By means of this mirror, the interference pattern formed during the process of wringing can be examined, and the completeness of the wringing controlled, depending, of course, on the surface finish of the gauge. The plate 25 also serves as a support for a cylindrical steel pipe, 30, into the upper end of which it is fitted and located by means of screws. This pipe, approximately coaxial with the central spindle 15, is about 22 in. long and 4 in. outside diameter.

The purpose of the outer pipe, in conjunction with a system of four diametrically opposing levers, 31, is to provide the necessary means for the adjustment of the working face of the quartz base-plane into perpendicularity with the mechanical axis of 15. The levers 31 are of cold rolled steel about 7 in. long, and are located on studs, 32, tapped into 30. The studs themselves are threaded to receive nuts, 33, with capstan heads. The nuts are spherically seated into mating steel washers, 34. Contact between the levers and the inner pipe 20 is maintained by four pointed struts, 35, which pass through oversize holes in the outer pipe, and are seated in conical depressions in the levers and inner pipe, respectively. The vertical distance between the struts and the lower screws 32, is about $\frac{1}{2}$ in. Hence for coarse adjustment, the lower nuts impart an approximate one-to-one motion to the lower end of the outer pipe, while the stalk 22 is strained from its original position. For fine adjustment, the upper nuts impart only about 1/12 of their axial movement to the lower end of the outer pipe.

When the instrument has been put into proper adjustment, the upper or working face of the quartz flat remains accurately perpendicular to the mechanical axis of the supporting spindle, as observed from the configuration of the interference pattern when the outer assembly is rotated. Although no particular care was taken to locate the steel ball 24 concentric with the axis of rotation of the stalk (and hence of the outer assembly), the rise and fall of the working face of the quartz flat is not greater than 2×10^{-5} in. about a mean plane, or a shift of two interference bands, for a complete turn of the outer pipe. This, of course, does not impair the accuracy of the instrument, as the measured parallelism is in no way affected.

Interpretation of Interference Patterns

A simple case, involving an end-gauge in which the short edges of the rectangular gauging faces are parallel to each other, will be considered.

(I) *Short Edge of the Upper Face of the End-gauge Initially Parallel to the Proof-plane*

Fig. 5 (*a*) is a schematic diagram showing an end-gauge wrung on to the working surface of the quartz flat 11. Above the gauge is shown the inclined optical flat 10. XY represents the long edge of the gauge's upper face, which is considered to be flat. In the position indicated, 10 has been so adjusted that the line of intersection of the plane of its lower surface (proof-plane) and the plane of the upper face of the end-gauge is parallel to the adjacent short edge of the gauge. When viewed through the eyepiece of the instrument, in monochromatic light (in this case, mercury green), the resulting interference pattern would appear as a series of equispaced parallel bands with the order of interference increasing from left to right, Fig. 5 (*b*). The direction of the order is easily determined by moving the appropriate tangent screw at the bottom of the supporting rod. It should be pointed out that the semi-reflecting mirror 9 turns the image upside down, but does not reverse it from left to right.

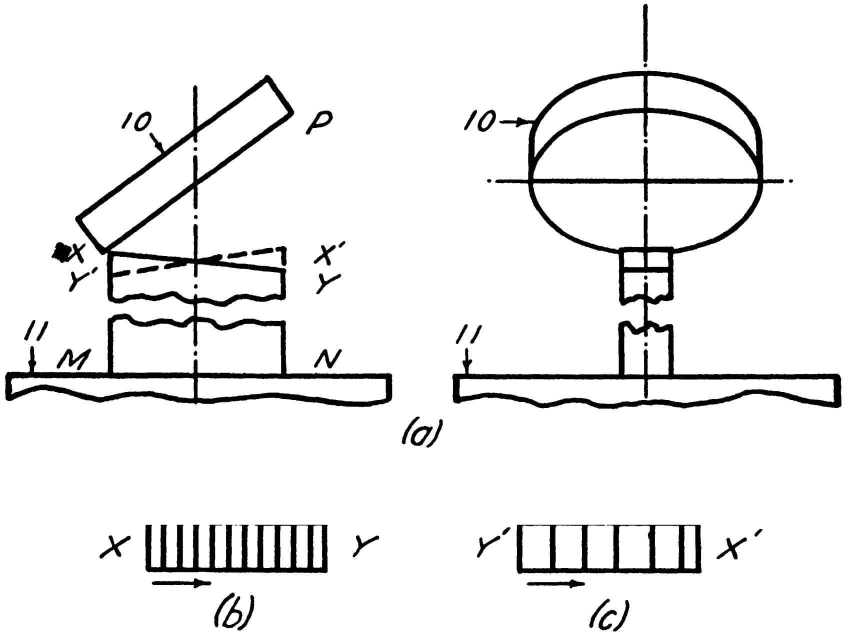

Fig. 5 (*a*) *Diagram showing a slightly wedge-shaped end-gauge with the short edge of the gauging face initially parallel to the proof-plane* (*b*) *The interference fringe system associated with the gauge in this position.* (*c*) *The fringe system associated with the gauge after rotation through 180°.*

From the theory, the angle *PXY* contained by the two planes concerned, is:

$$n_1 \lambda/2D \text{ radian} \qquad (1)$$

where n_1 is the number of interference bands (in this case 11.0) observed along the long dimension, D, of the working face of the end-gauge, and λ is the wave-length of the incident beam of monochromatic light (5460×10^{-7} mm. approximately, for mercury green light).

If now, the lower assembly on to which the end-gauge is wrung be rotated through 180°, the long edge will take up the position of the dotted line *X'Y'*, with the resulting interference pattern appearing as in Fig. 5 (*c*). In the same manner as above, the angle of inclination $PY'X'$ of the two planes concerned is:

$$n_2\ \lambda/2D \text{ radian} \tag{2}$$

where n_2 is the observed number (in this case, 5.4) of interference bands.

If, after this rotation, the order of interference increase from left to right, the angle contained by the planes of the upper and lower working faces of the end-gauge is given by half the *difference* of the two above expressions, i.e., by:

$$(n_1-n_2)\ \lambda/4D \text{ radian.} \tag{3}$$

Hence the side MX of the gauge is longer than the side NY by 3.0×10^{-5} in.

If, on the other hand, the order of interference after rotation, reverse, i.e., increase from right to left, the upper face of the end-gauge must have rotated in a vertical plane, through an angle greater than PXY. In this case, the contained angle between the upper and lower gauging faces would be given by half the *sum* of the two expressions, i.e., by:

$$(n_1+n_2)\ \lambda/4D \text{ radian} \tag{4}$$

and the side MX would be longer than the side NY by 8.8×10^{-5} in. When the quantity $(n_1 \pm n_2)$ is small, as it generally is, the accuracy of the test is not impaired if $\lambda/2$ be taken as 0.00001 in.

Figs. 6 (*a*) and 6 (*b*) illustrate the first condition described. They are actual photographs taken with the camera placed outside the peep hole of the instrument. In Fig. 6 (*a*), approximately 25 interference bands can be counted, while in Fig. 6 (*b*) there are about 22. Considering the order of interference to be increasing from left to right in both cases, Equation (3) applies, and it follows that as viewed in Fig. 6 (*a*), the left-hand side of the gauge is longer than the right by

$$(25 - 22)\ \lambda/4 = 1.5 \times 10^{-5} \text{ in. (approximately).}$$

The transverse line, shown in the photographs, is a reference line ruled in ink on the working face of the upper quartz flat.

(II) *Upper Face of the End-Gauge Initially Parallel to the Proof-plane*

The same result (again supposing that the gauge is out of parallel along the long dimension alone) as described in the first part of (I) may be obtained by operating the tangent screws at the bottom of the vertical rod to make the proof-plane initially parallel to the upper face of the end-gauge, as shown in Fig. 7 (*a*), and then, in the same manner as before, rotating the gauge through 180°. When the long edge, XY, is parallel to the proof-plane, no fringes will be observed on the face of the gauge (if the face be perfectly flat) when viewed in the instrument. When this edge is in the second position $X'Y'$, the resulting interference pattern would appear as in Fig. 7 (*b*), in which 5.6 bands are shown, with the order of interference increasing from left to right. From the argument in (I), it follows that the side MX is longer than the side NY by $5.6\lambda/4$ or nearly 3.0×10^{-5} in.

Owing to the fact that the working face of an end-gauge is never perfectly flat, the condition in which no interference bands appear can never actually be realized. Consequently, since the flat may be tilted slightly about a mean plane, and still apparently fulfil the condition of parallelism, the second method is not considered to be as sensitive as the first.

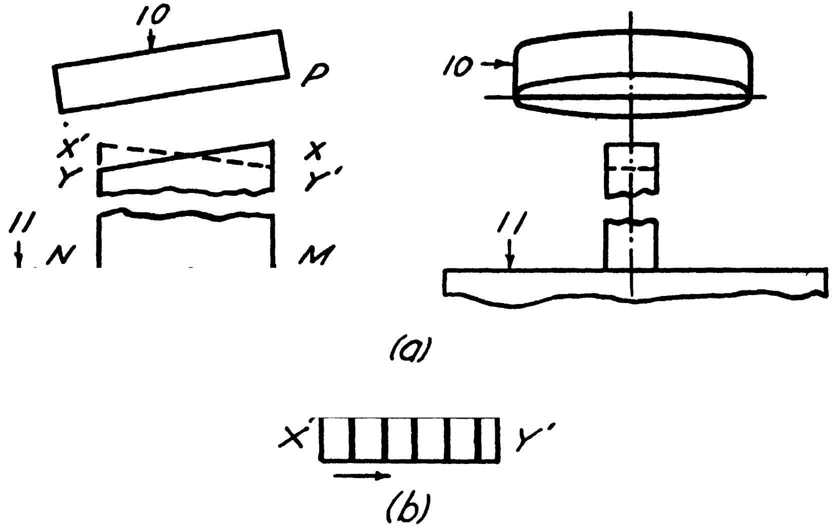

FIG 7 *(a) Diagram showing a wedge-shaped end gauge with its upper gauging face initially parallel to the proof plane (b) The interference fringe system associated with the gauge, after rotation through 180°*

(III) *Long Edge of the Upper Face of the End-gauge Initially Parallel to the Proof-plane*

A third case, in which the same results as in (I) and (II) above are found, may be obtained with another arrangement, indicated in Fig. 8. Fig. 8 (*a*) shows two elevation diagrams of the end-gauge with the proof-plane so inclined that it is parallel to the long edge but not to the short edge of the upper face of the gauge. The resulting interference fringe system would appear as in Fig. 8 (*b*), with the bands parallel to the long edge and with the order of interference increasing from left to right as shown by the arrow.

It can be seen that after rotation, the proof-plane will no longer be parallel to either edge of the gauge's upper surface; the interference system would then appear as in Fig. 8 (*c*). Here, inversion of the image by the semi-reflecting mirror is not considered. The direction of the increasing order of interference is shown by the arrows, and the number of bands intersecting the long edge is 5 6, while the number along the short edge is still the same as in Fig. 8 (*b*), since the angle contained by the proof-plane and this edge is unaltered. Hence, as before, the side MX is longer than the side NY by 3.0×10^{-6} in.

In general, the planes containing the two gauging faces of an end-gauge intersect in a line that is inclined to both edges of the faces. Therefore, the usual practice in determining the parallelism error is to follow the procedure outlined in (III), in which the long edge of the upper face is first made parallel to the proof-plane. The direction of the increasing order of interference is then noted, and the turntable rotated. The resulting interference bands will be skewed, more or less as in Fig. 8 (*c*), but not necessarily at the original angle or with the original spacing.

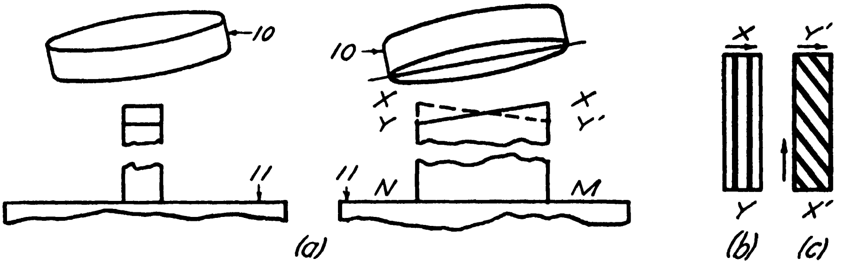

FIG. 8. *(a) Diagram showing the end-gauge with the long edge of the gauging face initially parallel to the proof-plane. (b) The interference fringe system associated with the gauge in this position. (c) The fringe system associated with the gauge after rotation.*

The interpretation now involves a combination of (I) in order to determine the parallelism error across the face (the same reasoning applies for either edge parallel to the proof-plane) and (III) to ascertain the error along the length of the face. In the case of the short dimension, i.e., parallelism error across the width, the number of bands intersecting the short edge and the direction of increasing order of interference are noted, and the parallelism error computed as in (I). In the case of the long dimension, the number of bands intersecting the long edge, and the direction of increasing order (taking into account the inversion of the direction of the order due to the mirror) are noted, and the error calculated as in (III).

Applications

The parallelism interferometer is not only useful as an instrument for assessing the parallelism error of end-gauges, particularly long ones, but it also has other uses. With it, the departure from flatness of an optically flat surface can be determined, and to a great extent the quality of the surface finish. It has also been employed as a vertical comparator in two ways:

(1) As an interferometer comparator, i.e., by the examination of the interference pattern formed in white and/or monochromatic light, between the proof-plane and the upper working surfaces of two adjacent end-gauges wrung to the quartz base plane.

(2) As a level comparator. This is described in some detail in the Appendix.

It is interesting to record that the parallelism interferometer was an indirect means of determining the absolute length of a 4 in. end-gauge of the Johansson type in a rather unique way. The gauge in question had been sent to the Metrology Section for the precise measurement of its length and for the assessment of parallelism and flatness errors. Photographs of the Haidinger fringes, obtained when the gauge was wrung to semi-aluminiumized quartz plates to form a Fabry and Perot étalon, were taken with krypton and cadmium as the light sources. First, an exposure was made by means of a Hilger spectrograph, with the étalon in such a position that the centre of the interference ring system was to one side of the gauge, about $\frac{5}{8}$ in. from its axis; then the étalon was moved parallel to itself until the ring centre was at the same distance on the other side of the gauge. The optical distance between the plates, in each position, was found by first measuring the diameters of the rings for each wave-length to determine the fractional order of interference, and then employing the 'method of coincidences'. The mean of the two lengths obtained, corrected for phase changes at reflection, gave the average mechanical length of the gauge plus two wringing film thicknesses, while the difference of the lengths was a measure of the parallelism error across the short face dimension.

The spectrograph plates yielded usable ring diameters in three adjacent colours, red to green, but because these wave-lengths were so close together the residuals of two distinct interference orders fitted each length equally well. This gave, in all, four possible independent lengths and consequently four parallelism errors.

The parallelism error of the end-gauge was thereupon measured by means of the parallelism interferometer. The value obtained gave the clue as to which two lengths should be utilized in the actual length determination. Subsequent independent checks of the length of the gauge revealed that the value indicated by the parallelism interferometer was the proper one.

APPENDIX

A Precision Level Comparator

A sensitive level vial is an excellent means for determining small differences in the lengths of end-gauges. Thus, if a level vial be substituted for the mount on the vertical supporting rod of the parallelism interferometer, the instrument may be used as a level comparator.

Description

A close-up view of the instrument is shown in the photograph, Fig. 9, while in Fig. 2, the level vial, swung out of its working position, is seen near the lower end of the tubular rod.

In the level comparator, the level vial is supported in an unstrained position in a cylindrical brass fitting, which is cut away, as shown in Fig. 9, for the purpose of viewing the bubble and graduations. Soldered to the bottom of the fitting is a rectangular brass block, into the lower face of which are peened two 0.125 in. hard steel balls, ½ inch apart and in line with the axis of the vial. The block is relieved by horizontal saw-cuts, and for adjustment purposes two fine-pitched screws are provided for straining the lower face in such a manner that the line of centres of the two balls can be made closely horizontal, when the bubble is in its central position. On to the top and at the centre of the upper surface of the fitting is soldered a smaller rectangular block, into which is inserted a hard steel pin. This pin is located between two parallel longitudinal hard steel knife-edges, acting as stops to limit the 'rolling' tendency of the level vial. The stops are fitted on to a brass block, carried on a movable arm of cold rolled steel. A saddle of thin brass sheet, which is also attached to the block, serves as a support for the level vial assembly; a portion of the saddle is cut away in order to receive the underneath block in which the balls are fitted. The movable arm is pivoted about a pin located in the side of a steel slider, which can be clamped at any desired height or position on the supporting rod of the parallelism interferometer. A screw, visible only in Fig. 2, butting against the top of the arm, serves to raise or lower the level assembly off or on the upper faces of the gauges being compared.

With the instrument are provided two precise level vials (made by Pessler, Germany) with attendant fittings and accessories. One of these vials has a sensitivity of 5 sec. of arc per division, while the other has a sensitivity of 15 sec. With the former it is possible to detect height differences to a precision of 0.000001 in. over a range of 0 0001 in., and with the latter, to about 0.000003 in. over a range of slightly more than 0.0002 in.

Operation

The method of operation is simple. The two end-gauges to be compared are wrung side by side, about 1/16 in. apart, on the quartz base-plate of the interferometer, and allowed to come to the same temperature. The slider is then clamped at a suitable position on the vertical rod, and the vial slowly lowered by means of the screw until the two balls rest on the respective faces of the gauges, and the cylindrical fitting is free of the saddle. Just before contact, the turntable should be rotated into such a position that the line of centres of the balls is approximately parallel to the short edges of the gauges. After allowing the vial to rest on the gauges for a time, both ends of the bubble are read. The balls are then lifted clear, the turntable rotated through 180°, and a second observation made. The bubble movement in conjunction with the calibration factor yields the difference in height of the two gauges.

Acknowledgments

The turntable assembly of the interferometer was designed by Mr. R. H. Field, Head of the Metrology Section, who also guided the design of the instrument as a whole. This unit, together with the level vial assembly, was constructed by Mr. A. A. Barks and his co-workers of the Supplementary

PLATE II

(a) (b)

FIG. 6 *Untouched photographs of interference fringes formed in the interferometer (a) and (b) correspond to (b) and (c), respectively of Fig 5 The heat effect, noticeable in the fringes and due to the non selectivity of the filters does not impair the practical accuracy of the measurement The heavy line across the centre of the gauge is a reference line ruled on the lower surface of the proof flat.*

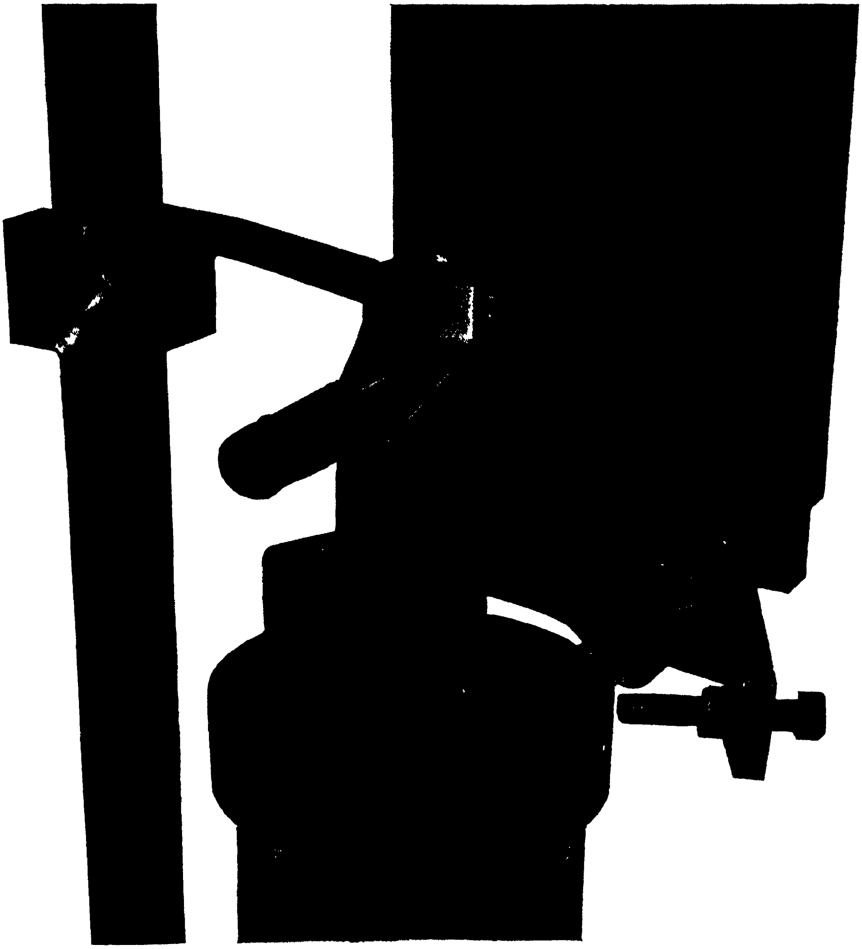

FIG. 9 *Close up view of the level vial and attachments used to convert the parallelism interferometer into a level comparator The mirror for determining the degree of the wringing of the gauges to the base plane can be seen below a pair of 3 in end gauges being compared*

Workshop of the Physics and Electrical Engineering Division. The interferometer mount and its supports were built in the Instrument Makers Wartime Training School, Dalhousie University, Halifax, N.S. Credit is due to Mr. J. N. Cairns, of the Optics Section, who succeeded in finishing the surfaces of the quartz flats to such a high degree of precision.

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PRODUCTION OF NITROGUANIDINE WITH HIGH BULK-DENSITY[1]

E. J. PRITCHARD[2] AND GEORGE F WRIGHT[3]

Abstract

Commercial nitroguanidine will not form pourable slurries in greater than 5 to 10% concentration because of unfavourable crystal shape. Controlled crystallization from water–methanol improves this crystal shape so that slurries containing equal parts of solid and vehicle can be poured.

Nitroguanidine is an explosive of power and detonation rate approximating that of T.N.T., while its extreme insensitiveness to impact and its higher true density (1.77) offer certain advantages over the commoner military explosive. Unfortunately these advantages have not heretofore been fully realizable. The production of nitroguanidine involves a final water crystallization from which the compound appears as finely felted needles of bulk-density less than 0.3.

The fineness and crystal shape of such nitroguanidine seriously limits the usefulness of this explosive. Firstly the low weight per unit volume presents a shipping and storing problem. Even when the explosive is packaged under pressure, the contents weighs less than one-third that of a comparable box of T.N.T. Secondly, although the rate of detonation of nitroguanidine is greater than that of T.N.T. at density 1.0 (5360 vs. 4870 m. per sec.), such highly compressed nitroguanidine is not easy to produce, whereas ordinary T.N.T. can be packed by hand to this density. The brisance, or shattering effect, of an explosive is dependent on its rate of detonation, which is, in turn, directly proportional to its packed density. In practical use, therefore, the hand-packed nitroguanidine at a density of about 0.3 has a rate of detonation not greater than 3000 m. per sec. This low rate not only limits its usefulness as a brisant high explosive but also tends toward incomplete detonation (with this type of explosive) unless the confinement is extreme.

A third disadvantage of the ordinary nitroguanidine arises because of the crystal shape. The interlocking tendency of the fine needles precludes the use of the explosive in a slurry which might be used for pouring into shell, bombs, or other containers, unless the percentage in the slurry does not exceed an ineffective 5 to 10% of nitroguanidine.

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[1] *Manuscript received January 28, 1947.*

Contribution from the Chemical Laboratory, University of Toronto, Toronto, Ont. This work was carried out at the request of the Department of Munitions and Supply.

[2] *Graduate student.*

[3] *Professor of Chemistry.*

We have found that the shape and size of the nitroguanidine crystal can be altered by crystallization from non-aqueous media to make it satisfactory in pourable slurries containing as much as 50% of the solid in liquid T.N.T. Thus, material of bulk-density 0.80 to 0.87 can be obtained by Soxhlet-extraction with hot solvent. Figs. 1, 2, and 3 are photomicrographic records of nitroguanidine crystallized from acetone, ethanol, and methanol, respectively. The crystals all had a refractive index of 1.526, identical with that of commercial nitroguanidine, and were mounted and photographed in a medium of refractive index 1.694 by Dr. W. C. McCrone of Cornell University. These 20-fold magnifications may be compared with the 100-fold magnification of a commercial nitroguanidine shown in Fig. 4 to show why the massive forms obtained from the non-aqueous solvents are more easily handled in bulk or in slurries than the felted needles produced from water. The extreme insolubility of nitroguanidine in these non-aqueous solvents does, however, make the extraction process so slow that it could have no practical importance. For the same reason a method involving alternate heating and cooling of a circulating slurry in these solvents was likewise unsuccessful.

What appears on the other hand to be a completely workable method of producing massive crystals involves the introduction of a hot saturated aqueous solution of nitroguanidine into methanol. Material with bulk-density as high as 0.96 has been produced in this manner in 90% yield per pass. The remainder of the nitroguanidine is not lost, since the methanol can be stripped from the mother liquor in a suitable still, to leave a hot aqueous residue which has been used for solution of a subsequent charge of crude nitroguanidine. One may expect that the quality of product will not be lowered by repeated re-use of the mother liquor, since evaporation of a portion to dryness gave a quantitative recovery of good nitroguanidine (m.p. 236° to 240° C.).

The superiority of this method over that of crystallization from water alone evidently depends on slow deposition over an appreciable temperature range from a dilute solution. These conditions are difficult to attain in water alone. Although nitroguanidine is much more soluble in water at the boiling point (1 part/11 parts water) than at 20° C. (1 part/375 parts of water) the greater part of this differential exists in the relatively narrow temperature range of 90° to 100° C. Indeed the rapidity with which crystallization of a saturated solution occurs in the range 96° to 100° C. caused us to decrease our initial concentration in boiling water to 1 part of nitroguanidine per 13 parts of water in order to prevent pipe-stoppage under conditions where the temperature of the conduit might drop several degrees.

The ideal medium for crystal growth is a water–methanol mixture varying from 1.2 to 1:1 parts by volume at a temperature close to the boiling point of pure methanol. This can be attained by rapid addition of the hot aqueous solution to pure methanol, initially at room temperature. A more gradual

PLATE I

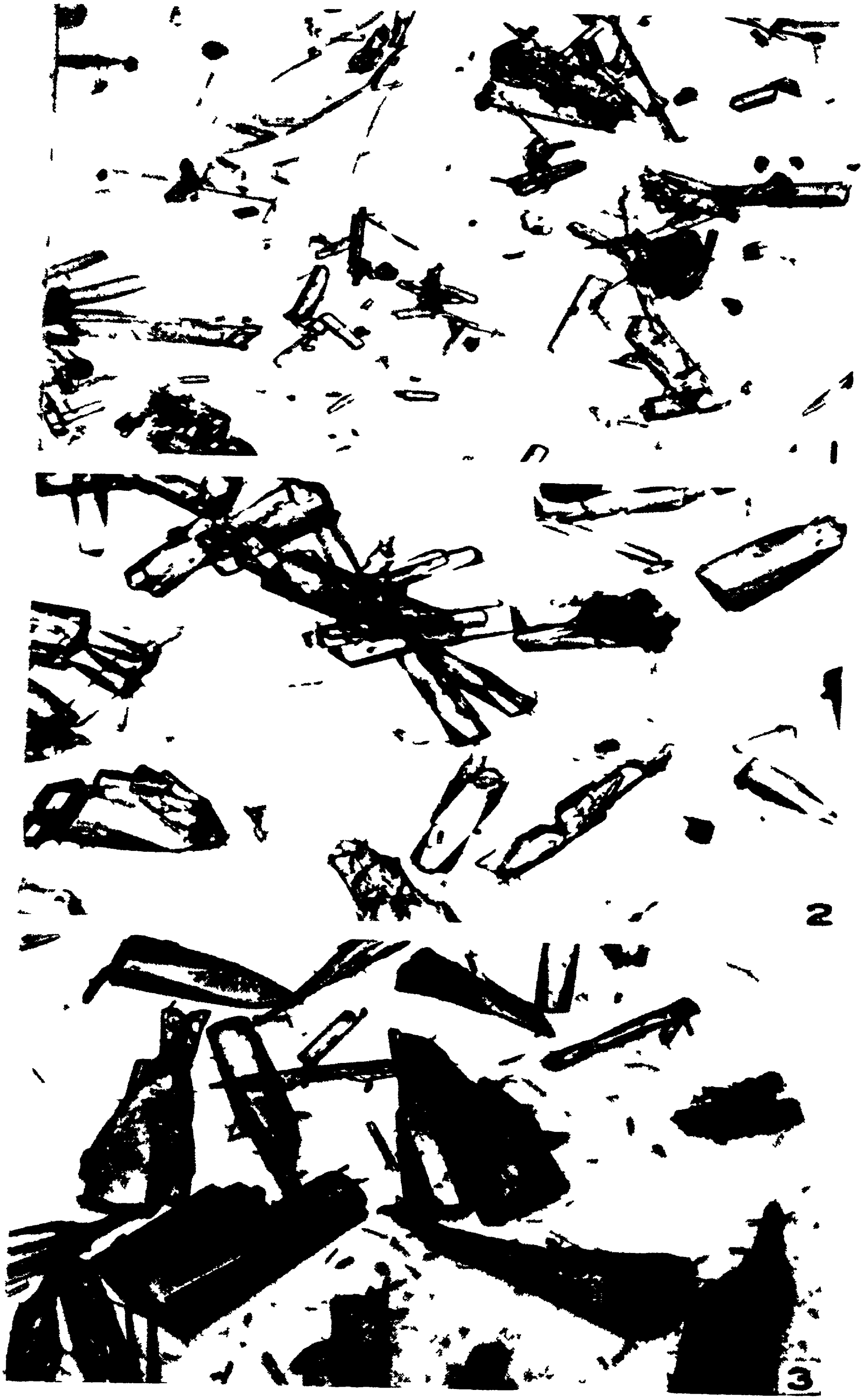
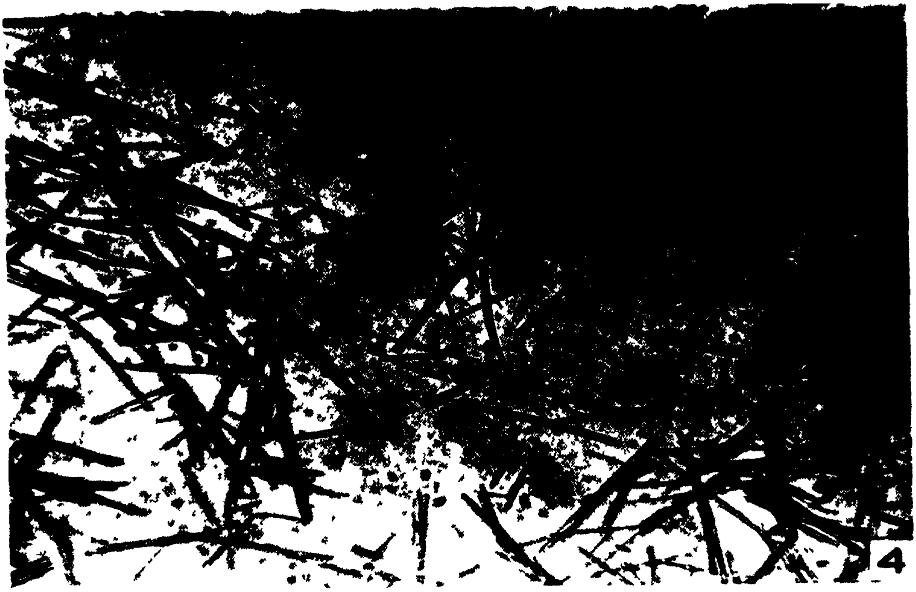


FIG. 1 *Nitroguanidine crystallized from acetone* 20 ×



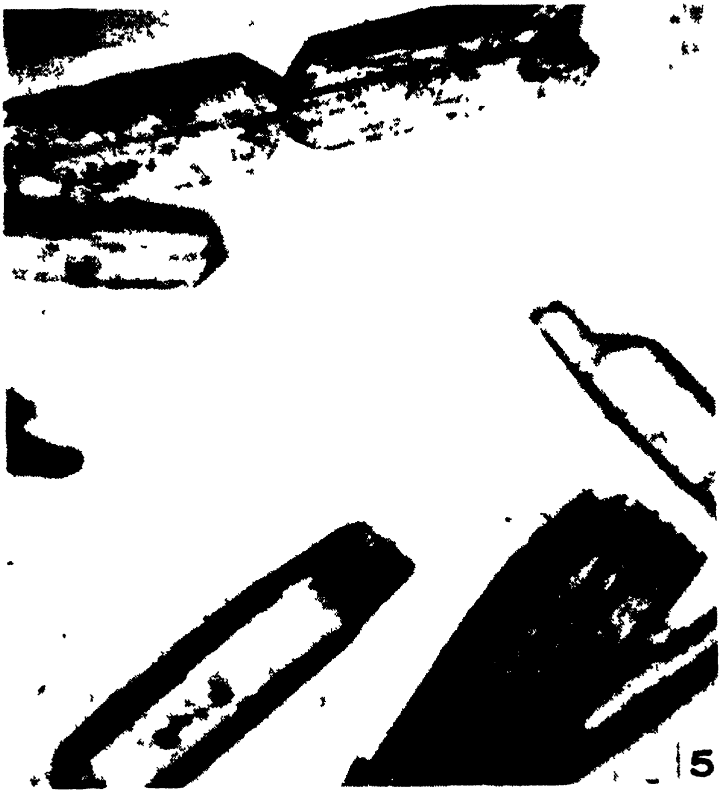


FIG. 4. *Commercial nitroguanidine.* × *100.*
FIG. 5. *Expt. 5 product on 60 mesh.* × *110.*

addition of the hot aqueous solution to the methanol gave a product having 4/5 the bulk-density of that obtained when the aqueous solution was added all at once. Since this result was not altered when the methanol was initially at 50° C. it would appear that temperature was less significant than the water–methanol ratio. Slow addition does of course impose a water–methanol ratio much higher than 1:2 at the beginning.

The experiments recorded in Table I were carried out by dissolving 600 gm. of nitroguanidine in 8000 cc. water in a paddle-stirred steam-jacketed stainless-steel vessel. This solution at 100° C. was run as rapidly as possible (four to six minutes) through a steam-jacketed delivery pipe into 16,000 cc. of methanol

TABLE I

VARIABLES IN NITROGUANIDINE CRYSTALLIZATION

To 16,000 cc. methanol were added one or more lots of 600 gm. nitroguanidine in 8000 cc. water

Expt. No.	Time for soln. of NG, min.	Orig. temp. in kettle, ° C.	Temp. after mixing, ° C.	Time air cooling, min.	Temp. after air cooling, ° C.	Time water cooling, min.	Temp. cooling water, ° C.	Fil-trate temp., ° C.	Bulk-density, loose	Bulk-density, packed	% Ppted.	Quality	Ratio $\frac{MeOH}{H_2O}$
1	5	25	64	210	34	25	7	10	0.59	0.71	86	G	2
2	5	20	63	55	50	35	7	10	0.63	0.83	87	F	2
3	5	27	66	60	50	35	7	12[1]					
3a	5	12	45	110	38	80	7	10	0.42	0.63	95	P	1
4	7	20	63	65	47								
4a	20	50	50	200	36	90	7	10	0.50	0.63	88	F	1
5	10	24	63	17	57								
5a	10	57	69	120	48	165	7	9	0.77	0.96	88	E	1
6	6	26	65										
6a	10	60	71										
6b	10	66	72	165	49	120	7	10	0.64	0.80	92	G	0.66
7	10	24	62	15	58								
7a	10	58	70	1260	24	—	—		0.60	0.79	84	G	1[2]
8	10	24	64	300	32	150	7	10	0.56	0.72	83	G	2[2]
9	10	33	65	30	61								
9a	10	61	71	0	—	30	40						
						30	25						
						30	15						
						30	7	10	0.53	0.65	91	F	1
10	10	25	63	19	57								
10a	10	57	68	10	62	15	38	49[1]					
						120	15	13[1]					
						60	7	10	0.55	0.70	91	F	1

[1] *These are not filtration temperatures, but are the temperatures reached at the end of the cooling period and just before the second addition.*

[2] *Recovered 99% methanol was used in these experiments.*

at 25° C. in a polished stainless-steel cylindrical kettle 13.5 in. in diameter by 22 in. high. The methanol was stirred by a $\frac{1}{4}$ h.p. 'Lightnin' stirrer equipped with two 3 in.-diameter three-bladed propellers turning at 1725 r.p.m. The resulting solution was then cooled with stirring to 9° to 12° C. according to the time schedules indicated in Table I.

The steam-jacketed kettle used for solution of nitroguanidine in water had a capacity of less than 2 gal., while a 12 gal. kettle was used for the crystallization operation. Since heat transfer from this latter kettle depended on cooling of the walls it was necessary to use sufficient methanol to give a 1:2 water–methanol solution after addition of the aqueous nitroguanidine solution was finished.

In order to obtain a final 1:1 water–methanol solution, the stirred slurry of crystallized nitroguanidine in the cooled 1:2 water–methanol solution was therefore treated with a second 600 gm. lot of nitroguanidine in 8000 cc. of water at 100° C. The cooling operation was then repeated as before. The quality of the crystals obtained by such duplication of the process was as good as that obtained when the final water–methanol ratio was 1:2.

These subsequent additions of hot aqueous nitroguanidine solution are shown in Table I by the letter *a*. In one case (Expt. 6*b*) a third aqueous nitroguanidine solution was added to the slurry. The initial and final temperatures of the slurry at the time that these additions were made are also shown in Table I.

The cooling operation was carried out in two steps. The first step was relatively slow and was accomplished simply, with our apparatus, as a spontaneous loss of heat to the air. This air-cooling was supplemented by a more rapid second step of water-cooling. This was effected by a water apron which surrounded the kettle. We found it was better to use warm water rather than cold for this operation; the use of cold water tended to cause surface crystallization on the walls of the stainless-steel kettle. This increased the proportion of fine nitroguanidine in the product.

The effect of variations in water–methanol ratio and in cooling schedule is shown in Table I by the correspondence in bulk-density (b.d.). The product was evaluated according to its loose bulk-density (weight per unit volume when poured into a 100 ml. graduated cylinder) and packed bulk-density (weight per unit volume after this same cylinder had been dropped 50 times from a height of 2.5 in. on to a leather pad).

A further classification of product is shown in Table I as Excellent, Good, Fair, and Poor. This classification is a composite one derived from two observations, which were found in most cases to correlate closely with one another. The first of these was crystal size and shape as determined by microscopic examination. Uniformity is desirable. Thus the material illustrated in Fig. 3 contains less aggregates than that shown in Fig. 2. The material shown in Fig. 3 is rated as excellent, while that shown in Fig. 2 is good, and that shown in Fig. 1 would be considered fair.

The ordinary water-crystallized nitroguanidine shown in Fig. 4 does not fit this microscopic classification in so far as its usefulness as an explosive is concerned. Thus it appears quite uniform under the microscope and it would on this basis deserve the classification 'excellent'. However, the microscopic examination does not show the actual occurrence as interlocking felted needles, because these are teased out on the microscope slide. This tendency toward 'felting' makes the material difficult to handle in bulk and it therefore deserves the classification 'poor'.

In order to supplement the microscopic examination, a pourability test was devised for inclusion in the classification, 'excellent' to 'poor', shown in Table I. Although pourability of nitroguanidine slurries in molten T.N.T. was of interest to us, we chose nitrobenzene instead, because it could be poured at a convenient temperature of 20° C. This test involved, firstly, the amount of nitrobenzene required to fill the voids (that is, to form a 'mush') and, secondly, the amount required in order that the resulting slurry would just pour from an inverted graduated cylinder after vigorous shaking.

Some classifications according to this test are shown in Table II as the number of cc. of nitrobenzene required in order that a slurry containing 2 gm. of nitroguanidine can be poured from a graduate. This evaluation conforms closely with that found by microscopic examination except in the instance, already mentioned, where interlocking of needles can occur. The dual evaluation has therefore been applied to the material obtained from the 10 experiments outlined in Table I.

TABLE II

POURABILITY OF NITROGUANIDINE SLURRIES

Type of sample	Bulk-density, packed	2 gm. nitroguanidine + cc. nitrobenzene		Qualitative classification
		To form mush	To form fluid	
Commercial nitroguanidine	0.25	4.2	>9	Very poor
Crystallization quickly from MeOH	0.37	3.4	4.3	Poor
Crystallization quickly from MeOH	0.42	2.3	3.0	Fair
Very slow crystallization, water–MeOH, 1 : 1	0.71	1.8	2.5	Good
Moderate crystallization, water–MeOH, 1 : 2	0.83	1.5	2.1	Excellent

The results in Table I show that the rate of crystallization is significant. There seems to be an optimum in the time of cooling, especially in the first step and this optimum must be close to that used in Expt. 5. This is brought out more clearly by Table III, where the screen analyses show that coarse material contributes adversely to high bulk-density. The contrast can be

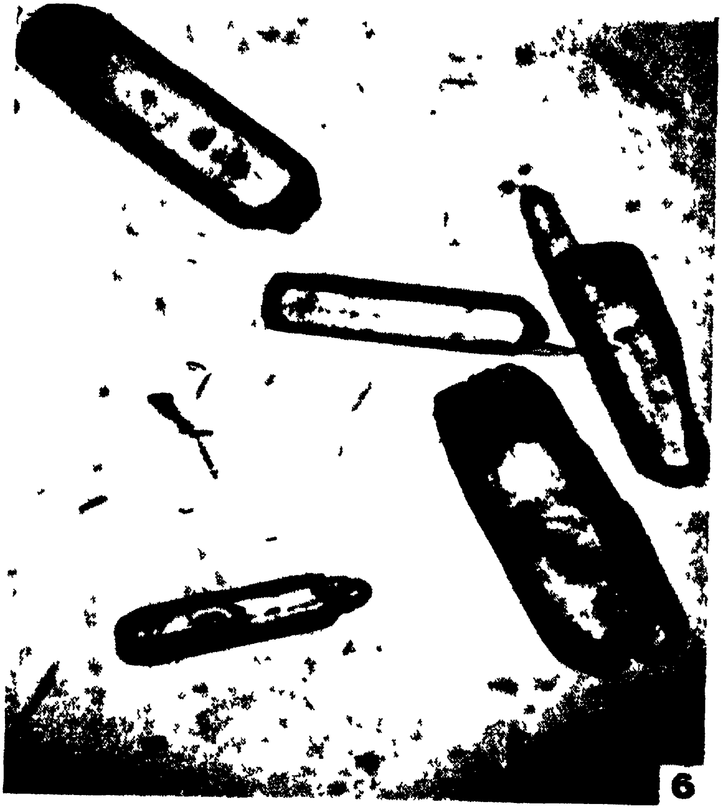
TABLE III

SCREEN ANALYSES OF HIGH DENSITY NITROGUANIDINE

Twenty-five gram samples poured into 100 ml. graduate (L, loose bulk-density, b.d.) and dropped 2.5 in. for 50 times (P, packed bulk-density)

Expt. No.	Screen cuts																					Over-all b.d. packed	Crystal shape
	On 20 mesh			On 40 mesh			On 60 mesh			On 80 mesh			On 100 mesh			On 150 mesh			Pass 150 mesh				
	%	b.d.		%	b.d.		%	b.d.		%	b.d.		%	b.d.		%	b.d.		%	b.d.			
		L	P		L	P		L	P		L	P		L	P		L	P		L	P		
1	0	0	0	7.8	.55	.69	51.2	.55	.69	17.7	59	.72	4.9	—	—	4.4	—	—	4.0	—	—	0.71	Smooth rods.
2	0	0	0	5.8	50	.59	51.6	.62	.72	19.1	.64	.80	8.7	—	—	9.2	—	—	5.4	—	—	0.83	Rough.
3	7.6	—	—	50.6	—	—	30.2	—	—	8.7	—	—	1.7	—	—	0.5	—	—	0.7	—	—	0.63	Non-homogeneous.
4	0	—	—	15.3	.41	.56	50.4	.50	.64	17.7	.55	.69	5.0	—	—	5.0	—	—	6.6	—	—	0.63	Irregular, long.
5	0	—	—	2.9	.66	—	26.0	.70	.76	33.8	.80	84	13.9	.84	.92	14.5	.84	.96	8.9	.66	.93	0.96	Rounded rods.
6	0	—	—	20.1	.51	.66	48.8	.62	.72	20.0	.59	.74	3.8	—	—	3.2	—	—	4.1	—	—	0.80	Irregular, long.
7	0	—	—	36.0	.62	.77	44.3	.59	.77	13.6	.55	.72	2.0	—	—	1.4	—	—	2.7	—	—	0.79	Regular.
8	0	—	—	11.8	.43	.57	61.0	.57	72	18.5	.57	.74	2.2	—	—	2.6	—	—	3.9	—	—	0.72	Irregular.
9	0	—	—	32.7	.43	.55	39.6	.50	.66	16.5	.52	.66	2.8	—	—	3.0	—	—	5.4	—	—	0.65	Long, jagged.
10	0	—	—	25.0	.52	.64	55.4	52	69	14.8	52	.69	1.0	—	—	1.2	—	—	2.6	—	—	0.70	Irregular, long.

PLATE III



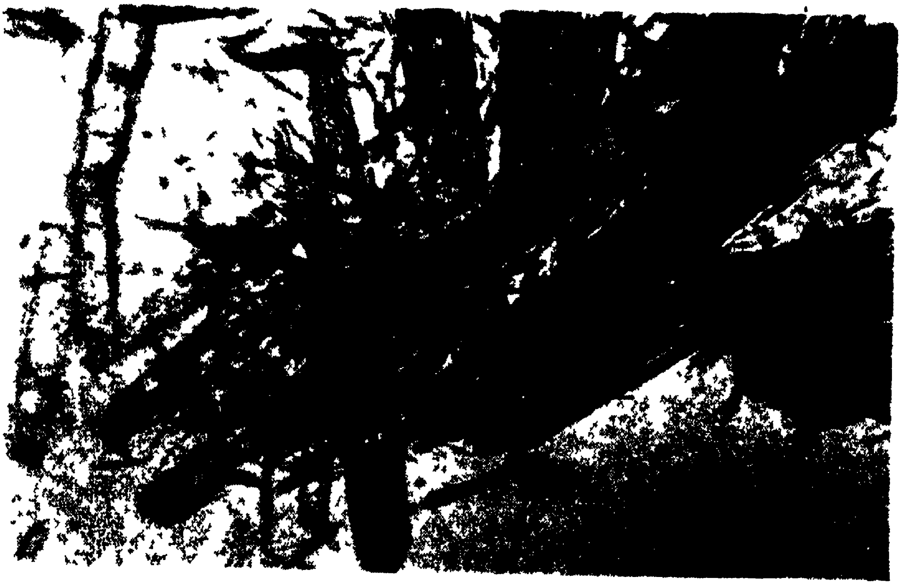


FIG 6 *Expt 5 product through 60 mesh* × *100*
FIG 7 *Expt 3 product* × *110*

made between Expt. 5 and any of Expts. 3, 7, 9, and 10. The effect of large size nitroguanidine crystals can also be demonstrated within Expt. 5 since the material through a 60 mesh screen gives a packed bulk-density of 1.0, while that retained on 60 mesh has a bulk-density of 0.67. When the latter, coarse fraction is rescreened, that retained on 60 mesh has a bulk-density of 0.85 while the material passing through 60 mesh has a bulk-density of 0.98. The effect of rescreening indicates that comminution is occurring during the operation, and this is confirmed by microscopic examination. Thus many of the coarse crystals in the material from Expt. 5 which are retained on 60 mesh show an apparent twinning such as is seen at the top in Fig. 5. That part passing through 60 mesh (Fig. 6) seems to be free from this type of twin.

The coarse screen fractions obtained from the experiments other than numbers 3 and 5 as shown in Table III also show clumped crystals such as is seen in Fig. 2. If such material is lightly ground under water, then its bulk-density and pourability are almost as good as those found for the material produced in Expt. 5. The difference is probably owing to the rounded ends of the ideal crystals shown in Fig. 6.

On the other hand, the material produced according to Expt. 3, Table I, is not materially improved by grinding. This is understandable after inspection of Fig. 7, a photomicrograph of the product. Such material is much better than commercial nitroguanidine with respect to bulk packing or pourability of slurries, but a T.N.T. slurry containing more than 30% of this material cannot be poured satisfactorily into high explosive shell. On the other hand, T.N.T. slurries containing 50% of the nitroguanidine produced according to Expt. 5 must be stirred during pouring to avoid segregation by settling of the solid phase.

In summary, a correlation of Tables I and II shows that a long cooling time for the methanol–water solution is undesirable, since it tends toward the formation of large crystal aggregates, which must be broken up by a subsequent operation. On the other hand the cooling may be too rapid, and this will lead to mixtures of crystal shapes obtained in Expt. 3. It is believed that a definite cooling schedule will have to be worked out anew for each installation, and Table I can only give a general idea of what this schedule would be. It would be advisable, therefore, to provide, in a large installation, a polished closed kettle with variable speed stirring and with provision for jacketed water-cooling over the range 65° to 10° C.

PRECISION OF LABORATORY MEASUREMENTS OF BREAKING STRENGTH OF TEXTILES[1]

By J. W. Hopkins[2] and Muriel W. Weatherburn[3]

Abstract

Warp breaking strength was measured in five test strips from each of a series of duplicate pieces of cotton duck in rotproofing experiments. Breaks occurring at the jaws of the machine, which amounted to some 16% of the total, gave results about 3.5% lower and 20% more variable than non-jaw breaks. Discrepancies in non-jaw breaks of similarly treated fabric arose partly from variance in test strips from the same piece and partly from additional variance between duplicate pieces. Weathering tended to reduce intra-piece, and soil burial to increase both intra- and inter-piece variability. The tests as conducted were capable of discriminating differences of the order of 15 to 20%. Greater gains in precision would have resulted from increasing the number of replicate pieces than from increasing the number of strips tested per piece in the same ratio. However, determination of the most economical test procedure for specified precision in each type of material also required consideration of the cost factor, which was nearly three times as great per piece as per strip.

Introduction

When the breaking strength of a fabric is estimated in accordance with the recommendations of the American Society for Testing Materials by measuring the breaking strength of 10 or more individual test strips, it is found that owing to variations in the performance of the testing machine, in the technique of the operator, or in the cloth itself, such measurements exhibit more or less fluctuation. Statistical examination of the results may consequently be necessary to ascertain whether the average obtained for any particular fabric differs significantly from a prescribed standard or from the averages for other fabrics. If all the averages to be compared are subject to variability of about the same extent, simple and powerful tests of significance are available in the procedure due to R. A. Fisher (1, 5) widely known under the name of 'analysis of variance'. If, however, the variance of measurements on different fabrics is unequal, tests of significance must take cognizance of this fact, if incorrect conclusions are to be avoided (3).

A recent paper by Edelman (4) has shown that the variance of a lengthy series of such measurements may be far from constant. However, whereas this author was mainly concerned with the acceptance testing of a large quantity of similar material by different operators, experimenters are more likely to have to deal with measurements made by a single operator, but relating to fabric whose characteristics have been subjected to modification. It is accordingly desired to describe here some statistical features of such measurements made in these laboratories.

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Contribution from the Division of Applied Biology and Division of Chemistry, National Research Laboratories, Ottawa. Paper No. 1 of the Special Committee on Applied Mathematical Statistics and N.R.C. No. 1569.

[2] *Biometrician.*

[3] *Chemist.*

Data

Data consisted of measurements of the warp breaking strength after exposure to leaching and soil burial by standard methods (2) and to outdoor weathering for four months at the National Research Laboratories, Ottawa, of unbleached cotton army duck (weight 10 oz. per sq. yd., thread count 46 three-ply warpwise and 37 two-ply weftwise per in.) treated with several series of rotproofing compounds. The experimental procedure adopted provided two random samples of fabric 6 in. warpwise by 8 in. weftwise representative of each treatment, for measurement of warp breaking strength after leaching and leaching followed by two and four weeks' soil burial, and after weathering and weathering followed by two and four weeks' soil burial. In the event, the effect of soil burial, particularly for four weeks, was so drastic as to make this determination impracticable in a number of instances; but with these exceptions five 6 by 1 in. ravelled warp strips from each 6 by 8 in. piece were broken in a motor-driven Scott D-8 tester, the initial jaw spacing being 3 in. and the rate of separation of the jaws about 12 in. per min.

Analysis

Jaw Breaks

It was reported by Edelman (4) that breaks at the jaws of the machine, comprising in his tests one-third of the whole, differed significantly in both average and variability from those occurring elsewhere along the test strip. This was attributed either to cutting action resulting from excessive tightening of the jaws, or to concentrated stresses in the fabric near the clamped portion due to uneven mounting. In an effort to minimize these adverse effects the jaws of the machine used here were coated with rubber, and this, together with care on the part of the operator, was perhaps reflected in the fact that the incidence of jaw breaks, namely 280 in 1715 or 16.3%, was only about half that noted above. These 280 jaw breaks were distributed over 354 sets of five measurements on separate pieces as follows: none in 158 (44.6%); one in 134 (37.9%); two in 43 (12.2%); three in 16 (4.5%); and four in 3 sets (0.8%). The observed numbers thus showed some approach to the calculated frequencies of 145.1, 141.6, 55.4, 10.9, 1.0, and 0.0 obtained by expansion of the binomial probability function

$$354(0.8367 + 0.1633)^5.$$

However, the actual frequency of zero and three or four significantly exceeded, while that of one or two fell short, of the random expectation for the total number of jaw breaks observed, suggesting some unevenness in the performance of the operator.

The undesirable attributes of these jaw breaks were likewise less pronounced than those reported by Edelman (4) for warp breaks of 116 W × 56 F cotton twill. Nevertheless, they still resulted in measurements that were on the average about 3.5% lower and 20% more variable than those obtained from the non-jaw breaks of test strips from the same pieces. Such aberrant observations occurring with variable frequency must clearly be excluded from averages that are to be compared without adjustment, and sufficient test material should accordingly be provided to make possible the required number of acceptable measurements.

Intra- and Inter-Piece Variance

Examination of the variation in breaking strength recorded for test strips from the same piece by the well-known 'control chart' method (8, 9) indicated that while this was reasonably uniform in all the pieces subjected to leaching only, it was definitely non-uniform in those undergoing weathering or soil burial.

Fig. 1 depicts the results for material leached subsequent to treatment but not otherwise modified, at which stage differences in treatment averages were of the order of 30% at most, and indicates that this series of measurements was 'in control' in the sense that it was characterized by uniform and predictable variability. The plotted points represent the range from maximum to minimum in non-jaw breaks of three test strips from each of 75 successive pieces, while the dashed lines indicate the limits, computed from tables due to E. S. Pearson (7), outside which only one point of this number would be expected to fall if measurements on all pieces were subject to the same Gaussian error system. In Figs. 2 to 4 the range in individual measurements is shown not in chronological sequence, but in relation to the average for each

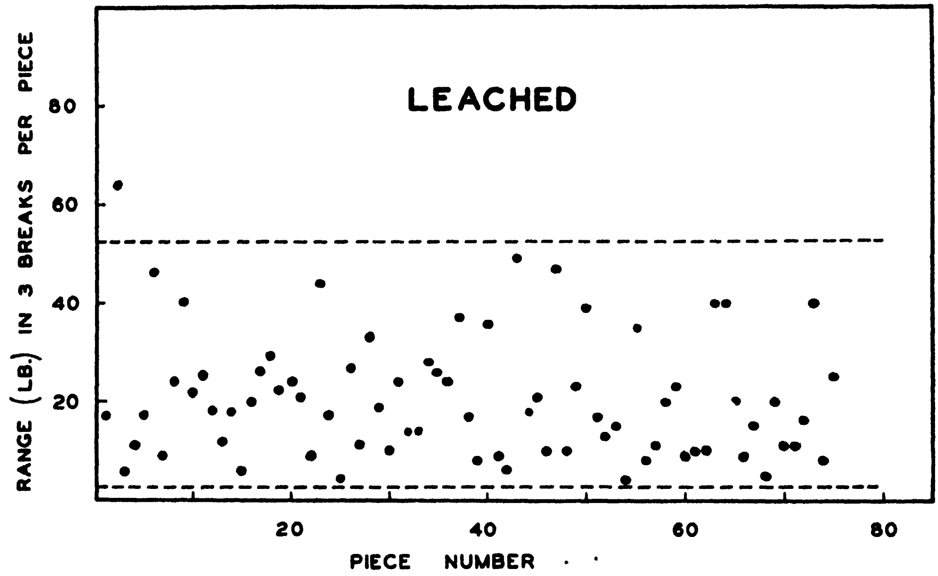

FIG. 1. *Range in breaking strength of three test strips (non-jaw breaks) from each of 75 pieces subjected to leaching following rotproofing treatment. Points represent observed ranges, dashed lines the theoretical limits within which all but one of these should fall.*

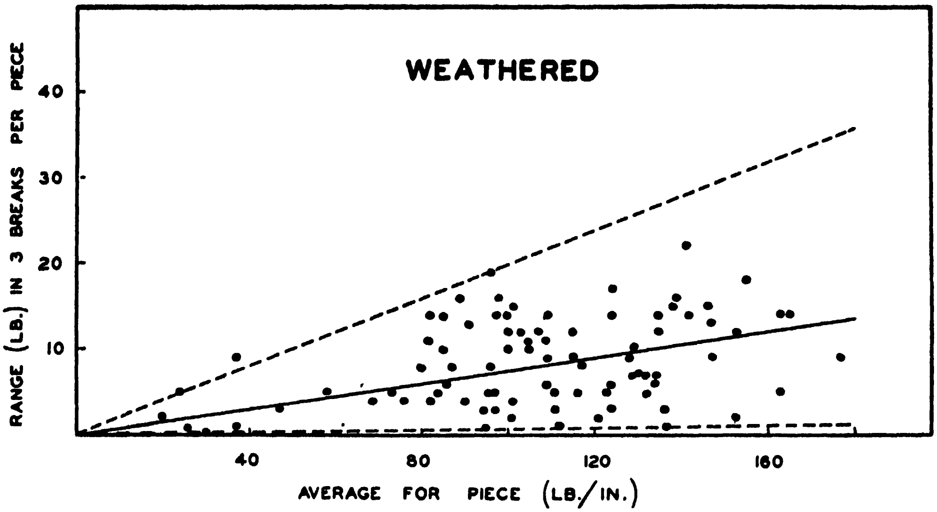

FIG. 2. *Range in breaking strength of three test strips (non-jaw breaks) in relation to average strength of pieces subjected to weathering following rotproofing treatment. Points represent observed ranges, dashed lines the theoretical limits within which all but one of these should fall.*

test piece, which now varied considerably. The divergence in measurements of pieces subjected to weathering only tended to increase progressively with the mean in the average ratio of 0.077 to 1, as illustrated in Fig. 2. On the other hand, after soil burial following either leaching (Fig. 3) or weathering (Fig. 4), test strips from pieces for which the average breaking force required

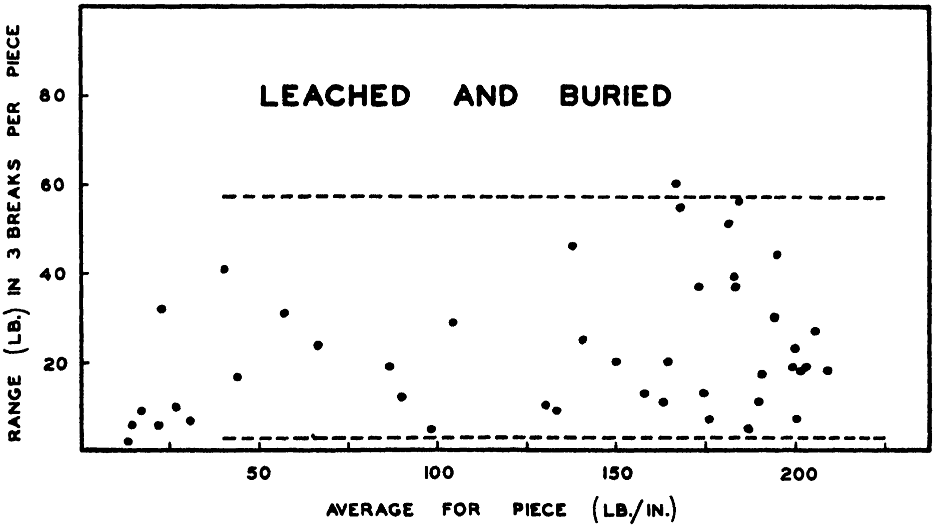

FIG. 3. *Range in breaking strength of three test strips (non-jaw breaks) in relation to average strength of pieces subjected to leaching and two weeks' soil burial following rotproofing treatment. Points represent observed ranges, dashed lines the theoretical limits within which all·but one of these should fall.*

was less than 30 lb. gave results in much closer mutual agreement than did those from the remaining majority. The variance of these latter was, however, sensibly uniform for averages of from 30 to 200 lb. These characteristics, also observed in earlier tests, may be explicable by the consideration that whereas weathering caused a fairly uniform degradation of the entire fabric, soil burial resulted in more patchy damage by localized aggregates of microorganisms. If these were distributed in accordance with Poisson's law (5), their variance would increase in proportion to their numbers, and thus might offset the reduction in variability due to general degradation of the fabric, except when the latter was so extensive as to restrict the possible range.

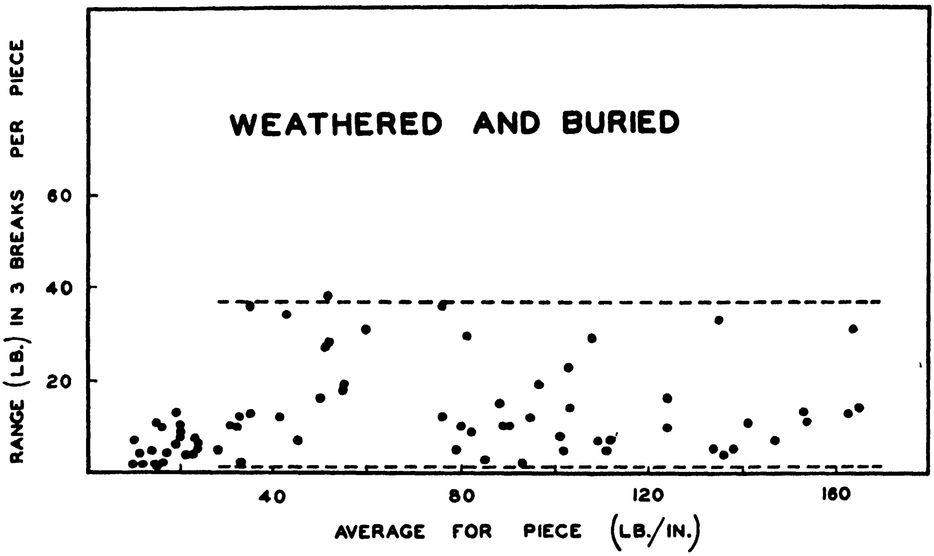

FIG. 4. *Range in breaking strength of three test strips (non-jaw breaks) in relation to average strength of pieces subjected to weathering and two weeks' soil burial following rot-proofing treatment. Points represent observed ranges, dashed lines the theoretical limits within which all but one of these should fall.*

The inter-piece variance of the averages for duplicate pieces subjected to the same treatment and exposure was also calculable, and was found to exceed $\frac{1}{3}$ the intra-piece variance of individual test strips in the ratio of 1.6 : 1, 2.8 : 1, and 4.7 : 1 for leached, leached and buried, and weathered and buried fabric respectively (excluding all pieces whose average strength did not exceed 30 lb. per in.). Comparisons of treatment averages were therefore subject to additional uncertainty from this cause.

Tests of Statistical Significance

The precision of treatment averages was affected firstly by the rejection of unacceptable (jaw break) measurements, and secondly by the inter- and intra-piece variance of the remaining data. On the seemingly justifiable assumption that discrepancies in the results for test strips from the same 6 by 8 in. piece originated for the most part in the experimental technique rather than in the cloth itself, the estimated variance (mean square error) of a treatment average derived from two test pieces providing n_1 and n_2 acceptable measurements was

$$\tfrac{1}{2}s_1^2 + \tfrac{1}{4}\cdot\frac{n_1 + n_2}{n_1 n_2}s_2^2$$

for an unweighted mean $\frac{1}{2}(\bar{x}_1 + \bar{x}_2)$ of the averages $\bar{x}_1$ and $\bar{x}_2$ for the two individual pieces;

$$\frac{1}{(n_1 + n_2)^2}\left((n_1^2 + n_2^2)\, s_1^2 + (n_1 + n_2)\, s_2^2\right)$$

for a mean $(n_1\bar{x}_1 + n_2\bar{x}_2)/(n_1 + n_2)$ weighted in proportion to the number of acceptable measurements for each piece; and

$$\left(\frac{1}{s_1^2 + s_2^2/n_1} + \frac{1}{s_1^2 + s_2^2/n_2}\right)^{-1}$$

for a mean weighted inversely in proportion to the estimated variance $(s_1^2 + s_2^2/n_1)$ and $(s_1^2 + s_2^2/n_2)$ of the averages $\bar{x}_1$ and $\bar{x}_2$. When $n_1 = n_2$, all three of the foregoing are equivalent. When $n_1 \neq n_2$, the third procedure gives, at the cost of some extra computation, the mean of least variance, while the first is preferable to the second if

$$s_1^2 > \frac{n_1 + n_2}{2n_1\, n_2}s_2^2 .$$

The values of s_1^2 and s_2^2 estimated from the data were:

	s_1^2	s_2^2
Leached	33.8	158.4
Weathered	20.6	0.002088 (mean)^2
Leached and buried 2 wk. (Average > 30 lb.)	150.7	254.2
Weathered " " " " " "	90.7	86.8

soil burial increasing the inter- and intra-piece variance of both leached and weathered material. From these, the variance of any treatment average was calculable by the formulae given in the preceding paragraph. The variance of the difference between any two averages was the sum of the variance of each, and from this the 'necessary difference' required for any specified degree of statistical significance was obtainable by taking the square root and multiplying by the appropriate probability factor (5). With five acceptable measurements on duplicate pieces for each treatment, the tests under consideration were found to be capable of discriminating differences of 17, 10, 21, and 16 lb. per in., in leached, weathered, leached and buried, and weathered and buried fabric at the 5% level of significance, the value cited for weathered material being that appropriate in the neighbourhood of the general average of 100 lb. per in.

Replication and Precision

From the foregoing estimates of s_1^2 and s_2^2, further estimates could be made of the variance of the averages of measurements of any specified number of pieces and test strips per piece, and hence of the differences in such averages required for statistical significance. The reciprocal of the last quantity provides an index of the estimated precision attained, and the relation of this to the number of pieces and of strips per piece of leached and of weathered and buried fabric tested is illustrated in Fig. 5. In consequence of the variance in test pieces additional to that in strips from the same piece, a greater gain in precision would have resulted from increasing the number of replicate pieces than from increasing the number of strips tested per piece in the same ratio.

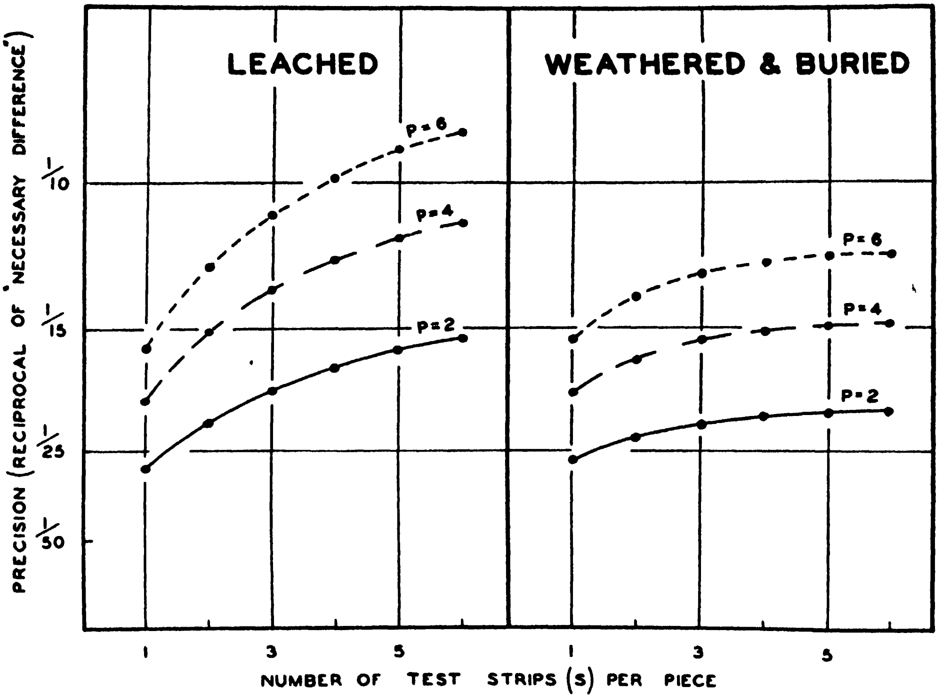

FIG. 5. *Estimated precision of averages in relation to number of replicate pieces (p) and of test strips (s) per piece.*

This consideration (discussed elsewhere by Mandel (6) in its relation to the replication of chemical analyses) was particularly operative in the results for weathered and buried cloth, which had a large inter-piece variance, and it was estimated that the average from two test strips from each of six pieces would have been 1.7 times as precise as that from six strips (the maximum number possible) from each of two pieces of this material. However, due weight must also be given to the fact that whilst the provision of each treated and exposed 6 by 8 in. piece entailed an average expenditure of about 12 cents for materials and labour, the cost of the labour involved in preparing and breaking a test strip averaged only about 4¾ cents. This resulted in cost in relation to the estimated precision to be obtained from different numbers of test pieces and strips varying as shown in Fig. 6. As inter-piece variance was the major source of discrepancy in measurements of weathered and buried fabric, any considerable improvement in the precision of these, if required, could be effected only by increasing the number of pieces, the devotion of labour to more than two test strips per piece being decidedly uneconomical. Moderate precision, corresponding to a 'necessary difference' of 15 or 16 lb. per in., could, however, have been obtained from either one test strip from each of six pieces or from two strips from each of four pieces subjected to leaching only. The latter would have required one-third more measurements, but in spite of this would have been 15% less costly in total materials and labour. These contrasting results emphasize the fact that quantitative study of the actual errors of measurement is prerequisite to assessment of the efficiency of test programs of this kind.

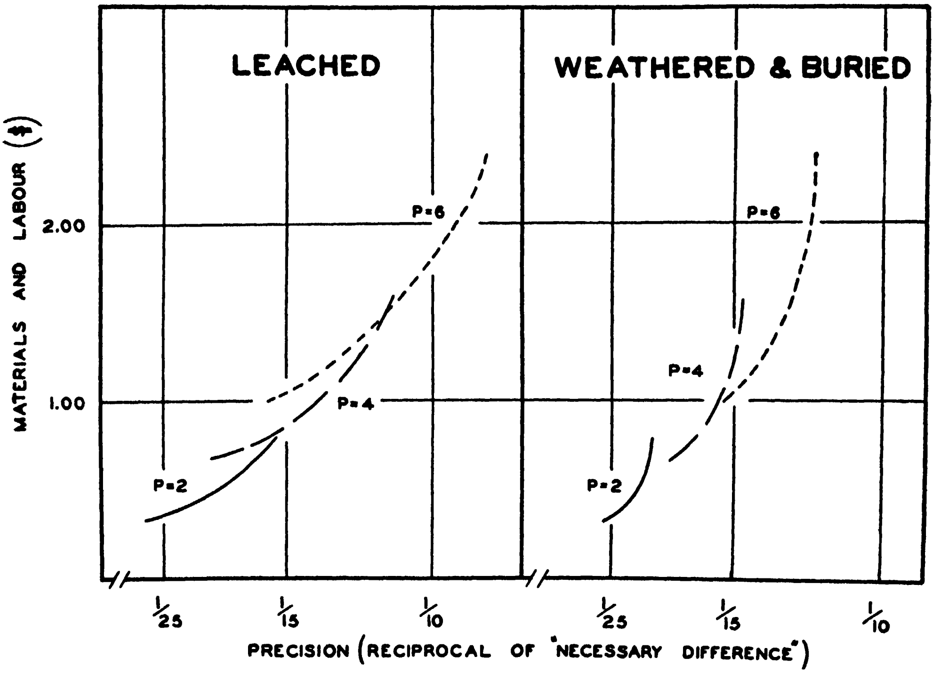

FIG. 6. *Estimated cost in relation to precision of tests using two, four, and six replicate pieces (p) and one to six test strips per piece.*

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XXII. THE EFFECT OF AEROBIC CONDITIONS ON THE *AEROBACILLUS* FERMENTATION[1]

BY DYSON ROSE[2]

Abstract

In the *A. polymyxa* fermentation, aerobic as compared to anaerobic conditions resulted in an increased yield of acetoin plus diol and a decreased yield of ethanol. As the fermentation proceeded under anaerobic conditions, there was a decrease in the proportion of substrate being used in the formation of acetoin and diol. This decrease was accompanied by an increase in the formation of acetic acid. During fermentation under aerobic conditions, no decrease occurred in the formation of acetoin plus diol.

Introduction

Walpole (10) in 1911 reported a greater yield of butanediol and acetoin from the fermentation of sucrose by *Bacillus lactis aerogenes* in the presence of oxygen than when the fermentation was conducted anaerobically. This observation has since been confirmed with other organisms inducing a similar fermentation, including *Aerobacter faeni* (2) and *Aerobacter aerogenes* (1), and a greater yield of these four-carbon compounds during the fermentation of milk under aerobic conditions has been observed by Prill and Hammer (7) and by other workers. The work of Kluyver *et al.* (5), and of Elion (3, 4), with yeast indicated that an acyloin condensation occurred whenever acetaldehyde accumulated in a fermenting medium, and that such an accumulation could be induced by supplying an alternate hydrogen acceptor. Oxygen was found to be capable of acting in this capacity and it was therefore assumed that the effect of oxygen in increasing the yield of butanediol and acetoin was the result of its action in preventing the reduction of acetaldehyde to ethanol.

In the yeast fermentations, ethanol is normally the only product obtained in large quantities and the above explanation for the increased formation of diol and acetoin under aerobic conditions appears to be satisfactory. However, in the more complex bacterial fermentations it is inadequate. In these bacterial fermentations hydrogen may be released in gaseous form and the

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reduction of acetaldehyde to ethanol need not occur even in the absence of an alternate hydrogen acceptor. It therefore cannot be assumed that the presence of such an acceptor would necessarily increase the total quantity of acetaldehyde accumulated. Furthermore, in these complex fermentations any acetaldehyde formed may be further metabolized in a variety of ways, and even under strictly anaerobic conditions considerable variation in the yields of the various products may occur (8) so that a decreased reduction of acetaldehyde to ethanol need not result in an increased yield of butanediol.

In view of these considerations and the probable importance of aeration in the commercial production of butanediol by means of the *Aerobacillus* fermentation, it seemed desirable to study the effects of oxygen more closely. The results of such studies on fermenting grain mashes have been presented by Adams (1); the present paper presents the results of similar studies using dextrose media.

Materials and Methods

The general procedures used in these studies were those previously described (8, 9). Two locally isolated strains of the organism, N.R.C. Strains C38 (2) and C25, were used. Efficient aeration of the medium was obtained by the use of Kluyver flasks, the purified oxygen or nitrogen being supplied at a rate of about 70 ml. per litre per minute.

The analytical methods have been described in previous papers (6, 8).

TABLE I

COMPARATIVE YIELDS OF THE VARIOUS FERMENTATION PRODUCTS UNDER AEROBIC AND ANAEROBIC CONDITIONS

Product	Yield, moles per 100 moles of dextrose fermented	
	Anaerobic	Aerobic
Butanediol	40.6	Trace
Acetoin	0.2	51.4
Ethanol	83.2	42.2
Formic acid	2.4	4.1
Acetic acid	6.3	7.4
Lactic acid	2.9	7.0
Succinic acid	1.6	2.5
Malic acid	0.2	1.5
CO_2	200.7	210.3
H_2	97.9	13.5
Acetone*	9.5	?
Carbon recovery	98.3%	92.7%
$\frac{\text{Acetoin + diol**}}{\text{Ethanol}}$	0.96	2.33
Oxidation-reduction index	1.00	2.14

* *The occurrence of acetone under these conditions has been discussed previously; the value given was obtained by calculation (8).*

** *Calculation on a weight basis.*

Yield of Products

Concurrent aerobic and anaerobic experiments were conducted to compare the yields of the various products. The results obtained under anaerobic conditions have been presented in a previous paper (8), and have been shown to be satisfactory by means of a balance sheet. Yield data for a representative aerobic fermentation with Strain C25 are presented in Table I.

These data show the expected increase in the yield of butanediol plus acetoin and also a distinct decrease in the production of ethanol under aerobic conditions. The production of organic acids by this organism is variable and the differences indicated in Table I are not believed to be significant. However, the increase in the production of carbon dioxide is probably a real effect of aeration. Adams (1) did not observe any decrease in the yield of fermentation products due to oxidation, but more thorough aeration was obtained with dextrose solutions than with the viscous grain mashes used by Adams. Carbon dioxide yields from dextrose were considerably in excess of the amount that would be produced by fermentation alone, but the extent to which oxidation occurs appears to be rather limited. The greatly reduced yield of hydrogen in the presence of oxygen indicates that oxygen was acting as a hydrogen acceptor, but the fact that some gaseous hydrogen was formed under aerobic conditions would seem to indicate that no well developed oxidative mechanism is present.

Rate of Formation of Products

Studies on the effects of oxygen on this fermentation were also made on samples withdrawn periodically. The presence of large amounts of dextrose together with the rapidly developing organisms made the determination of dextrose in the earlier samples difficult, and considerable error was thus introduced even though a clarification procedure was used. This error is clearly shown in the 'carbon accounted for' values of Table II where the excessively high values for the first samples are due to the error involved in the determination of dextrose. This error also resulted in a slight upward displacement of the first points of the curves of Fig. 1 (A and B) but did not obscure the shape of these curves.

Since wide variations in the yields of the main products of this fermentation have been observed (8), data are presented for two strains of the organism C38 (2) and C25. The first of these is the more typical in that the butanediol: ethanol ratio, on a weight basis, exceeded 1 : 1 under anaerobic conditions and the acetone yield was low or nil. The second, C25, produced larger quantities of ethanol than of butanediol under anaerobic conditions and may also have produced considerable quantities of acetone.

The yields of fermentation products, other than carbon dioxide and hydrogen, are presented in Tables II and III. Assuming that the fermentation involves the decarboxylation of pyruvic acid, and ignoring lactic and formic acids, a value of 400 moles should be obtained for the 'carbon accounted

TABLE II

THE YIELD OF PRODUCTS, AS MOLES PER 100 MOLES OF DEXTROSE UTILIZED, AT VARIOUS TIMES DURING ANAEROBIC FERMENTATION BY STRAINS C38 (2) AND C25

Sampling time (hr)	Butanediol	Acetoin	Ethanol	Formic acid	Acetic acid	Lactic acid	Succinic acid	Malic acid	Carbon accounted for*
C38 (2)									
12	60 0	34 4	108 9	59 8	27 6	11 5	4 6	1 1	767 7
24	54 5	14 0	80 5	18 9	6 8	4 3	1 8	0 3	488 8
36	44 5	13 3	76 0	8 3	10 5	3 6	1 7	0 3	431 3
48	44 1	7 1	73 8	2 6	16 6	3 3	1 7	0 1	405 3
72	52 6	4 3	63 3	2 8	21 2	3 2	1 4	0 1	415 0
96	50 4	7 0	60 9	2 9	20 8	2 5	1 0	0 4	409 0
C25									
12	46 7	29 0	169 5	90 0	74 3	17 8	6 6	1 5	966 2
24	21 8	8 8	91 3	16 5	20 8	4 5	2 5	0 7	389 4
36	20 3	6 1	85 3	5 8	20 4	3 7	2 0	0 5	343 9
48	16 6	5 1	98 4	6 3	20 2	3 5	1 7	0 2	348 4
72	18 0	0 8	93 8	0 6	18 9	2 4	1 6	0 4	316 4
96	19 9	1 3	89 6	0 9	18 6	2 5	1 6	1 2	320 8

* *Summation of (yield of product × number of carbon atoms in its molecule)*

TABLE III

THE YIELD OF PRODUCTS, AS MOLES PER 100 MOLES OF DEXTROSE UTILIZED, AT VARIOUS TIMES DURING AEROBIC FERMENTATION BY STRAINS C38 (2) AND C25

Sampling time (hr)	Butanediol	Acetoin	Ethanol	Formic acid	Acetic acid	Lactic acid	Succinic acid	Malic acid	Carbon accounted for*
C38 (2)									
24	12 1	25 9	26 4	12 6	35 6	10 9	4 6	8 6	374 1
48	33 1	25 9	45 9	24 1	24 5	9 0	2 4	1 0	441 5
72	24 3	34 6	38 2	3 4	9 3	4 9	2 0	1 5	362 7
96	18 9	46 5	40 8	2 5	7 8	5 4	2 3	1 3	391 9
120	0 6	62 9	41 4	3 2	8 3	6 4	2 2	—	384 6**
C25									
24	67 4	11 6	64 5	11 3	3 6	8 7	1 9	0 3	500 4
48	31 2	34 2	63 3	6 3	5 4	5 4	2 0	2 6	439 9
72	4 7	56 3	53 5	1 8	11 2	4 5	2 8	1 3	405 1
96	0	63 0	56 4	1 4	12 1	4 5	2 7	0 3	416 2

* *Summation of (yield of product × number of carbon atoms in its molecule).*
** *Malic acid sample lost.*

for' column. The values obtained under anaerobic conditions, apart from the initial errors in sugar analysis discussed above, are fairly satisfactory for Strain C38 (2) but are too low for Strain C25. This is probably due to the fact that acetone was not determined. Under aerobic conditions these 'carbon accounted for' values are in general quite satisfactory.

In Fig. 1 the yields, in millimoles per litre, of the various products are plotted against the millimoles of dextrose utilized so that the curves obtained indicate the *relative* rates at which each product was produced and also the proportion in which dextrose entered into the various products. In these figures the values for the four-carbon compounds, which are assumed to arise by condensation of two-carbon compounds, have been doubled in order to indicate the true proportionality among the products.

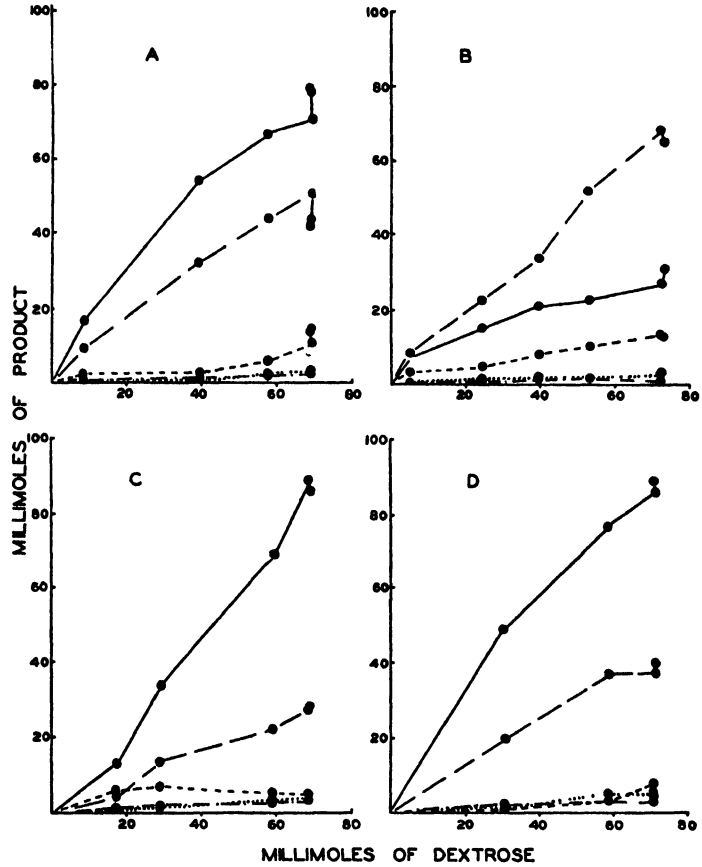

FIG. 1. *Millimoles per litre of product formed plotted against millimoles of dextrose utilized.* ———————— *2 (butanediol + acetoin);* — — — *ethanol:* - - - - *acetic acid;* — · — · — *lactic acid;* . . . . *2 (succinic + malic acid).*

A. C38 (2), anaerobic; analyses at 12, 24, 36, 48, 72, and 96 hr.; total dextrose available, 69.4 millimoles.

B. C25, anaerobic; analyses at 12, 24, 36, 48, 72, and 96 hr.; total dextrose available, 74.4 millimoles.

C. C38 (2), aerobic; analyses at 24, 48, 72, 96, and 120 hr.; total dextrose available, 69.2 millimoles.

D. C25, aerobic, analyses at 24, 48, 72, and 96 hr.; total dextrose available, 71.6 millimoles.

Note.—The yields of four carbon compounds have been multiplied by two in order to indicate the true proportionality in which triose particles (pyruvic acid) enter into the formation of the products.

Two different portions of these curves can be distinguished, the main sloping portions formed while the utilization of dextrose was proceeding and the small vertical sections that represent interconversion of the products after dextrose utilization was complete. These later portions of the curves indicate that small quantities of butanediol may be formed at the expense of ethanol but these interconversions among the products are of no significance in the present discussion.

Under anaerobic conditions the production of ethanol by both strains proceeded at the expense of a relatively constant proportion of the substrate as long as dextrose was present. With Strain C25 the production of ethanol utilized almost one-third of the carbon of the dextrose, an average of 0.92 moles of ethanol being obtained per mole of dextrose fermented. With Strain C38 (2) the yield of ethanol was lower and showed an average value of 0.71 moles per mole of dextrose. The production of butanediol plus acetoin, on the other hand, did not use a constant proportion of the substrate—the proportion decreased as the fermentation progressed. Apparently, during the later stages of the fermentation, more of a common precursor was diverted to the production of another product and less to the production of acetoin and diol.

The yields of succinic plus malic, and of lactic, acids were small and relativel constant, and they cannot account for the substrate diverted from the production of acetoin and diol. With Strain C38 (2) a distinct increase in the proportion of acetic acid formed occurred during the later part of the fermentation, and it is not improbable that this increment of acetic acid was formed at the expense of the acetoin. With Strain C25 none of the products shown in Fig. 1 increased sufficiently to account for the diverted substrate. Probably acetone, the only known product not included in these analyses, was produced to a greater extent late in the fermentation period. The low 'carbon accounted for' values of Table II support this suggestion.

Under aerobic conditions the relative proportion of precursor used in the formation of acetoin and butanediol was much increased, largely at the expense of ethanol. Moreover, each of these major products was produced from a relatively constant proportion of the dextrose utilized; the decline in the production of acetoin plus diol having apparently been prevented by the aerobic conditions. In the fermentation induced by Strain C38 (2) some decrease in the proportion of acetic acid formed is apparent and although the data are not conclusive there appears to have been a compensating increase in the acetoin plus diol yield. With Strain C25 a slight increase in the production of acetic acid occurred late in the fermentation period but this did not markedly detract from the acetoin plus diol yield. As noted above little acetone appeared to be produced under aerobic conditions. With both strains, all of the other acids were produced from relatively small and constant proportions of the substrate.

Conclusions

The data presented show that although in the presence of oxygen a small amount of the substrate may be oxidized to carbon dioxide and water, the main effect of aeration was to alter the proportions of the products. Thus, as frequently noted in the literature, the yield of acetoin plus diol was greater under aerobic conditions, while that of ethanol was lower. As the fermentation proceeded under anaerobic conditions, there was a decline in the formation of acetoin plus diol per mole of dextrose utilized, acetic acid or acetone apparently being formed in their place. This progressive change in the relative amount of substrate being converted to a particular product appears to be an important observation which, to the writer's knowledge, has not been previously recorded. It may presumably be related to some physical or chemical property of the medium or to the reproductive rate of the organism, but further study is required before any adequate explanation can be offered. The effect of oxygen in preventing the decline in butanediol plus acetoin production is also of considerable interest, both from the scientific and the practical point of view.

Acknowledgments

The author wishes to extend his sincere thanks to Dr. G. A. Adams and Dr. A. C. Neish for their advice and encouragement during the course of these investigations and to Mr. A. C. Blackwood for his assistance in maintaining the purity of the various strains of the organism.

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CHARACTERISTICS OF SOME PSYCHROPHYLIC BACTERIA[1]

BY J. J. R. CAMPBELL[2] AND G. B. REED[3]

Abstract

The 10 cultures of bacteria described in this paper developed in an acid (pH 5.0) digest of casein, stored at 4° C. Six of the 10 cultures were *Proteus ichthyosmius*, two *Pseudomonas schuylkilliensis*, one *P. fluorescens*, and one *Lactobacillus leichmanii*. The *Proteus* and *Pseudomonas* grow at 0° C. and the *Lactobacillus* at 0° to 5° C. With the exception of *Pseudomonas* there is no previous record of growth of these organisms at low temperatures.

In connection with another problem, tryptic digests of casein, adjusted to pH 5.0, were stored in carboys, without sterilization, in a cold room at 4° C. (3). The majority remained clear and apparently free from contamination for long periods. An occasional carboy of digest became contaminated. This contamination developed slowly but the initially clear digest became cloudy from the growth in about two weeks. From one such contaminated digest some four species of bacteria were isolated. As a result of the conditions under which they developed and certain unusual properties of the organisms it seemed desirable to record their characteristics.

The organisms were isolated and cultivated in a basal medium composed of 1.0% tryptic digest of casein, 0.5% yeast extract, and 0.5% dipotassium hydrogen phosphate. In experiments where the ability to use a specific substrate was not being tested 0.1% glucose was added to the basal medium. To determine the ability of organisms to grow at temperatures below freezing, agar stabs, 4.0% sodium chloride broth, and 10.0% glycerol broth were used. All three proved satisfactory at −5° C. In determining temperatures of growth the tubes of media were held at incubation temperature for six to seven hours prior to inoculation. In order to determine the optimum pH and the optimum temperature of growth, nephelometer readings were carried out every eight hours. The conditions favouring maximum growth at 24 hr. were considered optimum. In general, the same relative results were obtained at 8, 16, and 24 hr.

Since we were interested in these organisms that could grow under the unusual conditions of pH 5.0 and temperature of 4° C., isolations were made on agar plates at pH 5.0 streaked with the contaminated casein digest and incubated at 4° C. Colonies, which were fully developed at two weeks, were remarkably uniform and gave the impression that only two species were present. However, 10 colonies, which included the slightest variation in colony form, were picked. These isolates were examined in some detail.

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[1] *Manuscript received April 8, 1947.*

Contribution from the Department of Dairying, the University of British Columbia, Vancouver, B.C., and Department of Bacteriology, Queen's University, Kingston, Ont.

[2] *Associate Professor of Dairying, the University of British Columbia.*

[3] *Professor of Bacteriology, Queen's University.*

Six of the 10 cultures were identified as a species of *Proteus;* three cultures as three species of *Pseudomonas*, and one culture as a *Lactobacillus*. The somewhat unusual characteristics of the four species are summarized in the following paragraphs.

Proteus sp.

Rods: 0.5 to 0.8 by 1.0 to 2.0 μ, occurring singly. Motile with peritrichous flagella. Gram-negative.
Gelatine stab: Liquefaction.
Agar colonies: Large, white, entire, shiny, raised.
Broth: Slightly floccular with thin pellicle.
Litmus milk: Slight acid production. Rapid peptonization. Litmus reduced.
Indole not formed.
Nitrites produced from nitrates.
H_2S formed.
Acid and gas from dextrose, sucrose, maltose, and mannitol. Lactose not fermented.
Methyl red test negative; Voges-Proskaeur test positive.
Temperature relations: Optimum 20° to 25° C.
Minimum below −5° C.
Maximum 35° to 40° C.
Optimum pH: 6.5 to 8.0. Will initiate growth at pH 5.0.
Salt tolerance: Will grow in up to 9.0% sodium chloride.

This organism appears to be *Proteus ichthyosmius* (Hammer) Bergey *et al.* It differs from the accepted characteristics of the species in the absence of indole formation, in the appearance of colonies on agar, and the absence of fishy odour in milk cultures. However, in view of the very limited amount of work done on *P. ichthyosmius*, it seems more logical to regard the present organism as a member of this species rather than as a new species.

There is no previous record that this species grows at low temperature. Moreover, growth at −5° C. appears to constitute a new low temperature record for the genus *Proteus*.

Pseudomonas schuylkilliensis

Rods: 0.5 to 0.7 by 1.5 to 3.0 μ. Motile with polar flagella. Gram-negative.
Gelatine stab: Liquefaction at one week.
Agar colonies: Flat, opaque, smooth, 1 mm. in diameter.
Broth: Slightly flocçulant with light pellicle.
Litmus milk: Slight acid. Digested from the surface down.
Indole not formed.
H_2S not produced.
Nitrates not reduced.
Aerobic.
Pyocyanin produced.

Fluorescent pigment produced.
Temperature relations: Optimum 27° C.
Minimum 0° to 5° C.
Maximum 35° C.
Optimum pH: 7.0. Will initiate growth at pH 5.0.
Salt tolerance: Will grow in up to 6.0% sodium chloride.

Pseudomonas fluorescens

Rods: 0.5 to 0.7 by 1.5 to 2.5 μ. Motile with polar flagella. Gram-negative.
Gelatine stab: Rapid liquefaction.
Agar colonies: Brownish, raised, smooth.
Broth: Heavy sediment with thin pellicle.
Litmus milk: No coagulation. Digestion from the surface down.
Indole not formed.
H_2S not produced.
Nitrites and nitrogen produced from nitrates.
Aerobic.
Pyocyanin not produced.
Fluorescent pigment produced.
Temperature relations: Optimum 25° C.
Minimum below −5° C.
Maximum 37° C.
Optimum pH: 6.8. Will initiate growth at pH 5.0.
Salt tolerance: Will grow in up to 6.0% sodium chloride.

These two pseudomonas forms show the accepted characteristics of *P. fluorescens* and *P. schuylkilliensis*. There are many previous records of low temperature growth of various species of *Pseudomonas*, Hess (2), Thjøtta and Sømme (4). Gibbons (1) isolated *P. fluorescens* from most iced fish fillets examined. Many strains of both species were found to grow rapidly at 0° to 3° C.

Lactobacillus sp.

Rods: 0.3 by 1.0 to 3.0 μ, occurring singly, in pairs, or in short chains. Non-motile. Gram-positive.
Catalase negative.
Agar colonies: Pin-point, white.
Agar slant: Very faint growth.
Broth: Uniformly turbid with heavy growth.
Litmus milk: Completely reduced in 10 hr. No further action. Trace of acid formed in yeast milk.
Gelatine not liquefied.
Nitrites not produced from nitrates.
Acid from dextrose, sucrose, and maltose. Lactose and inulin not fermented. Produces only traces of by-products other than lactic acid from dextrose. Inactive lactic acid formed.

Temperature relations: Optimum 20° to 25° C.
Minimum 0° to 5° C.
Maximum 37° to 40° C.
Optimum pH: 6.5. Will initiate growth at pH 5.0.
Salt tolerance: Will grow in up to 7.0% sodium chloride.

The range of conditions under which this organism grows is most unusual for a lactobacillus. The fact that it rapidly reduces litmus milk without fermenting lactose seems paradoxical; however, when yeast extract is added to litmus milk there is a slight increase in titratable acidity. If this organism is regarded as a non-lactose fermenter it fits into the description of *L. leichmanii* Bergey *et al.* except that the optimum temperature range for growth is much lower than that recorded for *L. leichmanii.*

Discussion

These four species of bacteria, found growing under conditions of unusually low temperature and unusually high acidity, appear to fit into the descriptions of previously known species except for the low optimum and especially the low minimum temperatures at which they grow.

There is no evidence of how these organisms got into the low temperature stored digests. Since the cold room had been used for this purpose for two to three years it is possible that they are the product of variation and acclimatization, from more mesophilic types, to low temperature and high acidity.

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THE STABILITY OF CYANOGEN CHLORIDE[1]

By A. B. Van Cleave[2] and R. L. Eager[3]

Abstract

The stability of cyanogen chloride in contact with Pyrex glass, aluminium, bakelite, brass, and steel at 20° C. has been investigated. The tests indicate that crude or purified cyanogen chloride can be satisfactorily and safely stored in contact with any of these materials except brass, provided that precautions are taken to ensure that only relatively small amounts of water or hydrochloric acid are present. Brass has been shown to be entirely unsatisfactory as a container material for either crude or pure cyanogen chloride as it appears to catalyse a decomposition reaction that is not shown by any of the other materials tested.

Introduction

In the commercial preparation of cyanogen chloride from a cyanide and chlorine, it is probable that small amounts of water, hydrogen cyanide, chlorine, and hydrogen chloride would be present as impurities. Jennings and Scott (1), in discussing the methods of preparation of cyanogen chloride, state that the pure product does not polymerize but that impure products show a varying degree of polymerization, depending upon the conditions. They found this to be especially marked when traces of hydrochloric acid were present. Whitmore (4) states that cyanogen chloride polymerizes on standing to give cyanuric chloride $(CNCl)_3$. It is also known that cyanogen chloride undergoes hydrolysis in alkaline media to produce cyanates but the literature does not contain any direct reference to hydrolysis in acid media.

According to Sartori (2) cyanogen chloride has no corrosive action on iron, lead, aluminium, tin, or silver but it does attack copper and brass slightly, with the formation of a protective coating that prevents further corrosion. No reference to the original literature is given and in view of certain other conflicting information it is desirable to study the storage characteristics of cyanogen chloride in contact with various materials suitable for the manufacture of containers.

Materials

Cyanogen Chloride

Except where noted, crude cyanogen chloride (American Cyanamid Company), which had been filtered through glass wool to remove polymerized materials and solid ammonium chloride, was used. The original liquid was slightly yellow in colour and some yellowish white solid had collected on the walls of the containers. An analysis based on the amount of chloride present after complete hydrolysis by sodium hydroxide indicated the crude liquid to be 99.4% cyanogen chloride.

Some of the crude cyanogen chloride was purified by distilling it from a mixture of cuprous chloride, magnesium oxide, zinc oxide, and calcium

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[1] *Manuscript received January 27, 1947.*
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.

[2] *Associate Professor of Chemistry.*

[3] *Graduate student.*

chloride. This material had a freezing point of approximately −7° C. and was water white. Analysis by the above mentioned method gave a mean value for duplicate samples of 100.1% cyanogen chloride.

Metal Samples

Sheet brass and aluminium were used. The steel was band steel. Two coats of bakelite varnish were applied to some of the steel samples so as to ensure that the substrate was entirely covered.

Experimental Method

Since it was desired to measure the pressure increase, if any, the samples were arranged in clean Pyrex glass vessels as indicated in Fig. 1. To facilitate the measuring of pressures from approximately zero to the neighbourhood of four atmospheres, a U-shaped mercury manometer with air enclosed in the sealed off limb was used. The metal samples were cleaned, dried, and weighed and then sealed into the reaction bulbs. Before admitting the cyanogen chloride, the manometers were calibrated by taking readings of known pressures.

About 25 ml. of crude cyanogen chloride was poured into the reaction bulb (which was immersed in a freezing mixture) at *G* (Fig. 1) by allowing it to

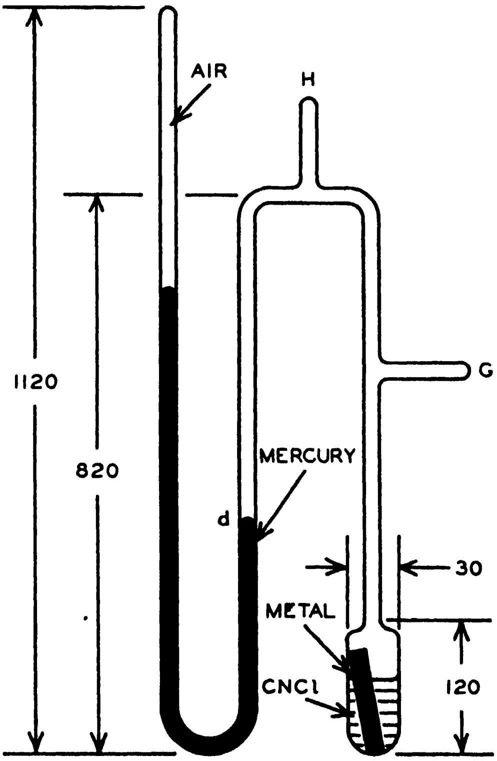

Fig. 1. *Diagram of apparatus used to measure the pressure increase.*

run through a funnel packed with Pyrex glass wool. Following the addition of cyanogen chloride the apparatus was sealed to a vacuum system at *H* (Fig. 1) and evacuated. When evacuated to as low a pressure as possible, the pumps were cut off, the low temperature bath removed, and the cyanogen chloride allowed to melt. When all the solid had melted, it was frozen once more and again evacuated. These operations were intended to remove any inert gases present. The apparatus was sealed off from the vacuum system and placed in a constant temperature bath maintained at 20.0 ± 0.1° C.

When purified cyanogen chloride was being used the above procedure was modified in that the material was distilled into the evacuated apparatus through phosphorus pentoxide.

In order to prevent condensation of liquid cyanogen chloride on the mercury surface at *d* (Fig. 1), which occurred when the room temperature dropped below 20° C., a heater consisting of nichrome wire wound on a strip of transit board was placed along the row of manometers. This heater was shut off for some hours before pressure readings were taken, thus ensuring that the enclosed air in the manometers would be at room temperature when the readings were taken, which was at intervals of approximately one week.

After being in progress for the time indicated in Table I, or Fig. 3, each test was terminated as follows: the reaction vessel was removed from the bath and placed in a dry ice – acetone freezing mixture. When the pressure became steady the glass above *d* (Fig. 1) was thickened, drawn down, and sealed off from the manometer. The reaction vessel was then allowed to come to room temperature, causing the pressure to rise above atmospheric. The tip was then broken beneath the surface of a barium hydroxide solution. The formation of a heavy white precipitate was taken to be a positive test for carbon dioxide in the escaping gases.

The metal strips were then removed, examined for corrosion, and weighed.

Experimental Results

The results may conveniently be considered in two parts:

(*a*) blank tests and tests with metals other than brass, and

(*b*) tests with brass.

(*a*). The blank tests together with tests involving aluminium, steel, and bakelite coated steel with both crude and purified cyanogen chloride are summarized in Table I. In tests Nos. 17 and 18 no manometers were attached; these tests were started as checks on Nos. 10 and 11, in which the manometers were broken by accident. Fig. 2 gives a graphical representation of any pressure change that occurred in those tests where manometers were attached. To avoid undue complication of this figure the results of only one of each duplicate test has been plotted using a few representative pressure readings. In all cases the results of duplicate tests were similar. It is to be noted that in all cases where crude cyanogen chloride was used, including the blanks, some pressure increase was shown over a long period of time. In no case,

TABLE I

SUMMARY OF CHANGES OCCURRING IN THE BLANKS AND TESTS WITH METALS OTHER THAN BRASS

Test No.	Metal	Time in days	Original weight, gm.	Final weight, gm.	Changes occurring in liquid	Change in appearance of metal strips	Result of CO_2 test
2	Al	580	2.2222	2 2172	Very little change. Original yellow colour had deepened slightly. Very small quantity of grey coloured ppt.	No apparent change	Positive
3	Al	558	2 3581	2.3895	Same as No. 2	No apparent change except that in the vapour space a few fine white crystals had deposited on the edges	Positive
4	Al using purified CNCl	270	2 2040	2 2041	The CNCl remained water white, no sign of polymerization	Same as No. 3	Negative
16	Al using purified CNCl	270	2 2031	2 2031	Same as No. 4	No apparent change	Negative
10	Steel	152	37 3090	37 2425	Final appearance not known definitely as water entered from the bath but there had been no pronounced change		
11	Steel	209	36 1590	36.1410	Same as No 10		
17	Steel	143	33 1839	33 2018	Same as No. 2	Attacked very slightly, some darkening of the surface. Part of metal in vapour phase mottled yellow	No test made
18	Steel	143	33 5768	33 7043	Same as No. 2	Same as No. 17	No test made
12	Blank (Pyrex glass)	427			Same as No. 2		Positive
15	Blank (Pyrex glass)	551			Same as No. 2		Positive
13	Bakelite	547	40 7974	40.8961	Same as No. 2	Bakelite not attacked. On the surface of the bakelite in contact with the liquid a few small dark coloured specks had formed	Positive
14	Bakelite	398	36.1165	36.2360	Same as No. 2	Same as No. 13	Positive

however, was the pressure increase excessive or likely to lead to an explosion. The metals used in the tests showed very little evidence of corrosion and this is borne out by the fact that only insignificant changes in weight occurred. Small amounts of polymer were present in most of these tests, but certainly most of the original cyanogen chloride was still present when the tests were terminated.

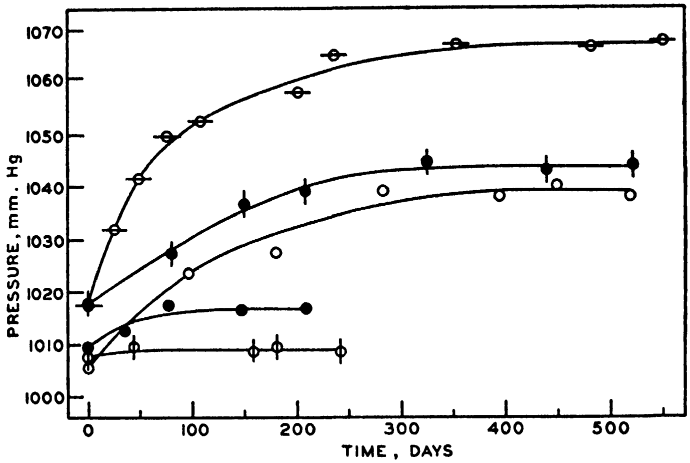

FIG. 2. *The increase of pressure with time.*
-⊖- = *Aluminium, No. 3;* ⧫ = *blank, No. 15;* ○ = *bakelite, No. 13;*
● = *steel, No. 11;* ⌽ = *aluminium, No. 4 with pure cyanogen chloride.*

(*b*). The variation of pressure with time for the tests involving brass is shown in Fig. 3. In test No. 5 (Fig. 3) purified cyanogen chloride was used while in tests Nos. 8 and 9 the crude material was used. In all three cases the liquid darkened in a comparatively short time and a dark brown precipitate settled out. In test No. 9 practically complete solidification occurred in about 250 days. The falling off of the pressure in this case was no doubt due to the complete polymerization or reaction of the cyanogen chloride. Examination of the solid material remaining showed it to consist mainly of a dark brown substance in which was embedded a few white crystals. A small quantity of a dark viscous liquid remained. A few of the white crystals were separated from the mass and tests indicated them to be identical with polymerized cyanogen chloride as obtained by Van Cleave and Mitton (3).

The part of the remaining solid that was soluble in water gave qualitative tests for NH_4^+, Cl^-, and Cu^{++} ions. The bulk of the dark brown material was not identified.

Complete solidification of the cyanogen chloride had not occurred in tests Nos. 5 and 8 up to the time of their termination. The liquid that remained on the termination of these tests was dark coloured and viscous and a con-

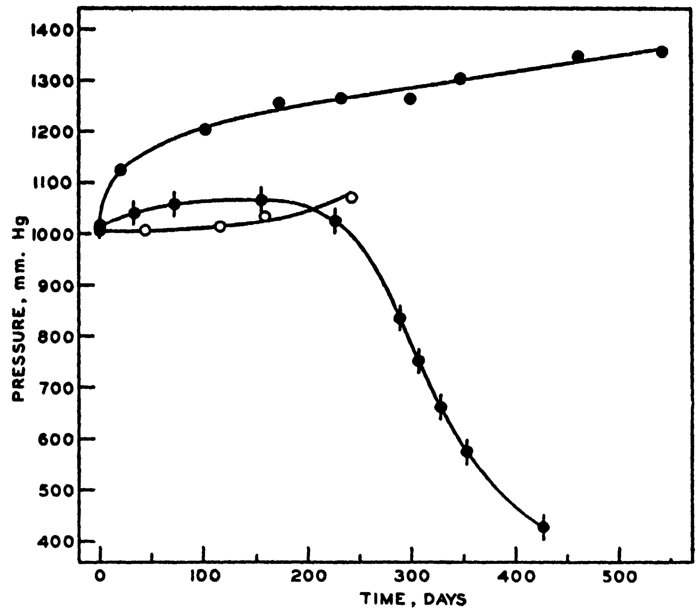

FIG. 3. *The variation of pressure with time for samples in contact with brass.*
● = *No. 8;* ϕ = *No. 9;* ○ = *No. 5 with pure cyanogen chloride.*

siderable quantity of a dark coloured solid had collected in each tube. In all cases the brass strips showed evidence of extensive corrosion. These tests indicate brass to be entirely unsuitable for use as a container for either crude or pure cyanogen chloride.

Discussion

The results show that a reaction leading to a pressure increase occurred in all cases, including the blanks, where crude cyanogen chloride was used. However, it was only in the case of samples in contact with brass that the pressure reached undesirable proportions at 20° C.

It has been shown (3) that the reaction

$$CNCl + 2H_2O \rightarrow CO_2 + NH_4Cl$$

proceeds readily in the presence of hydrochloric acid. Hence, if the crude cyanogen chloride contained small amounts of water and acid, this would be a likely reaction to occur in these tests and would account for the pressure increases observed. This is supported by the positive tests for carbon dioxide as noted in Table I. It is only necessary to assume about 0.10% of water in the original samples to account for the pressure increases. In all cases, except where brass was used, the pressure has tended towards a constant value after a period of approximately 10 months. After that time there was no significant change in any of the tests involving aluminium, bakelite, steel, or the blanks. Apparently, it took a considerable time for all the water impurity to be used up at 20° C. owing to the low concentration of acid impurities present. It is likely that this phase of the reaction would be more rapid at elevated temperatures, but there is no reason to believe that the pressure increase would have reached dangerous proportions at any ordinary storage temperature. It should be noted that no increase in pressure occurred in tests Nos. 4 and 16 (aluminium in contact with purified cyanogen chloride) over a period of 270 days nor was there any evidence of polymerization. This seems to bear out the statement that pure cyanogen chloride is quite stable.

The only test in which the pressure increase could not be accounted for on the basis of the above proposed reaction is No. 5 (brass in contact with pure cyanogen chloride). This test showed no significant pressure increase for about 60 days. After that, however, a steady pressure increase was shown and marked decomposition of the liquid cyanogen chloride became evident. It appears that brass catalyses the decomposition of even purified cyanogen chloride with the evolution of a gas. This gas was not definitely identified. The rather large pressure increase shown in test No. 8, Fig. 3, may be partly due to this decomposition reaction. However, the major part of the pressure increase in this case was probably due to the reaction of cyanogen chloride with a few drops of water that were accidentally introduced during the process of sealing the manometer off from the vacuum system.

Conclusions

The tests indicate that crude or purified cyanogen chloride can be satisfactorily and safely stored in contact with Pyrex glass, aluminium, bakelite, or steel at 20° C., provided that precautions are taken to ensure that only relatively small amounts of water and acids, such as hydrochloric acid, are present.

Brass has been shown to be entirely unsatisfactory as a container material for either crude or purified cyanogen chloride as it appears to catalyse some decomposition reaction that is not shown by any of the other materials tested.

Acknowledgment

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DRIED WHOLE EGG POWDER

XXVII. FURTHER OBSERVATIONS ON THE OCCURRENCE OF *SALMONELLA* ORGANISMS IN CANADIAN POWDER[1]

By N. E. Gibbons[2]

Abstract

During 1945, *Salmonella* organisms (other than *S. pullorum*) were isolated from 112 of 400 samples (28.0%) of Canadian dried egg powder. Fourteen types were found: *S. oranienburg*, *S. typhimurium*, *S. thompson*, *S. montevideo*, *S. newington*, *S. bareilly*, *S. manhattan*, *S. potsdam*, *S. anatum*, *S. newport*, *S. paratyphi B* (tartrate positive), *S. bredeney*, *S. tennessee*, and *S. selandia* (listed in order of prevalence). *S. pullorum* was isolated from 17 samples. In the majority of samples the most probable number of organisms was less than one per gram. No *Salmonella* organisms were found on the shells of 12,276 commercial eggs; *Salmonella* were isolated from the shells of eight of 24 eggs and later from the meats of two of 144 eggs from infected flocks.

Introduction

Previous studies indicated that *Salmonella* types were present in Canadian dried egg powder produced during 1943 (6). In November, 1944, it was suggested that this survey be resumed. Consequently all plain dried egg powders produced from the latter part of November, 1944, to the end of December, 1945, were examined. By this time four plants were producing dried sugar–egg powder (1, 11) and as most of the others were preparing to produce this type of powder, the survey was discontinued. Since dried sugar–egg powder is used exclusively for baking purposes there should be no health hazard (3, 7).

The present paper summarizes the findings of this study. The result of some incidental work on the source of these organisms is also reported.

Materials and Methods

Composite samples of powder from each carlot of powder produced were sent to a central control laboratory where they were thoroughly mixed under aseptic conditions for bacteriological and chemical analyses (12). Approximately 60-gm. portions of this mixed material were placed in sterile bottles, stored at approximately 40° F., and collected weekly for examination. Only Grade *A* powders were examined.

The methods used have been reported previously (6). Quadruplicate 5 gm. portions were examined throughout the study. From July on, both Difco SS and bismuth sulphite agars were used. Starting in September, whenever the first examination (total 20 gm.) was negative, the remainder of

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the powder (usually 30 to 40 gm.) was cultured. Preliminary identification was made by means of O-sera and fermentation reactions. All cultures identified as *Salmonella* were typed by Dr. P. R. Edwards of the Salmonella Centre, Lexington, Ky.

The most probable number of organisms per gram of powder was determined for a number of samples (6). It was observed that even when three of four 5-gm. lots were positive the M.P.N. was usually less than one per gram. Hence in the latter part of the work, estimates were made only if all the quadruplicate portions were positive.

Results

From the latter part of November, 1944, until Dec. 31, 1945, samples from 400 carlots of powder were examined and *Salmonella* types (other than *S. pullorum*) isolated from 112 (28%). This is five times the incidence reported previously (6). *S. pullorum* was found in 17 samples.

The distribution by plants is shown in Table I. As before, there was no relation between the finding of *Salmonella* organisms and the plate count or total microscopic count of individual carlots, as given in the official reports of the Special Products Board. Rather there were indications of a contamination carried over in the plant. On several occasions, two, three, or even four carlots in succession would contain the same type.

TABLE I

DISTRIBUTION BY PLANTS OF SAMPLES OF POWDER POSITIVE FOR *Salmonella* TYPES OTHER THAN *S. pullorum*, ARRANGED IN ORDER OF PREVALENCE

Plant	Carlots examined	Lots positive	Percentage positive	Average bacterial content thousands/gm.	
				Plate	Microscopic
Western					
I	59	40	67.8	110	2550
H	79	24	30.4	76	720
G	35	9	25.7	74	670
A	13	3	23.1	39	2000
B	62	11	17.7	16	520
K	4	0	0	37	320
	252	87	34.5		
Eastern					
F	27	6	22.2	120	580
C	63	11	17.4	275	1400
E	50	8	16.0	50	2900
D	8	0	0	65	18,350
	148	25	16.8		
Total	400	112	28.0		

If average plate counts over the whole period are taken there is some relation with the incidence of *Salmonella* in the western plants (Table I). There is also some relation with direct microscopic counts. This relation is not as apparent with the eastern plants. Plant *D* operated practically entirely with frozen melange and pasteurized all liquid egg.

There is no apparent relation between the type of drier and the incidence of *Salmonella* organisms. Plants *I* and *H* are very similar in design and the powder is removed rapidly. Plants *B* and *E* are also similar in design and operation, and have about the same incidence. It is also true that the eastern plants *F* and *C* operate at higher temperatures than the western plants. Plant *C* began to use a preheater in March, 1945, and no *Salmonella* organisms were isolated during the period April to December. This was the only preheater used in Canada during the period under review and the results confirm the findings of Schneider (15). However, it is our opinion that the number of contaminated eggs is greater in Western Canada and that this in relation to plant operation determines the incidence and survival of *Salmonella* organisms. This opinion has not been substantiated, as very little experimental work has been done.

The distribution with time is shown in Table II. In this series a few more lots were positive in the fall and winter months than in the summer. This is the opposite of the previous series (6). On the over-all basis, the percentage of positive samples was remarkably constant throughout the year. The few positives in March and April are believed due to laboratory conditions.

TABLE II

DISTRIBUTION OF *Salmonella*-POSITIVE SAMPLES BY MONTHS

Month	From western plants			From eastern plants			Total		
	Carlots examined	Lots positive	Percentage positive	Carlots examined	Lots positive	Percentage positive	Carlots examined	Lots positive	Percentage positive
Nov	5	1	20.0	3	2	66.6	8	3	37.5
Dec	19	7	36.8	13	6	46.1	32	13	40.6
Jan	25	9	36.0	14	4	28.6	39	13	33.3
Feb	24	9	37.5	15	4	26.6	39	13	33.3
March	25	2	8.0	17	1	5.8	42	3	7.1
April	22	3	13.6	13	0	0	35	3	8.6
May	21	7	33.3	14	2	14.3	35	9	25.7
June	24	8	33.3	10	0	0	34	8	23.5
July	19	4	21.0	11	0	0	30	4	13.3
Aug	15	8 (10)[1]	53.3 (66.6)	11	0	0	26	8 (10)	30.8 (38.4)
Sept.	14	5 (7)	35.7 (50.0)	7	0	0	21	5 (7)	23.8 (33.3)
Oct	13	5 (7)	38.4 (53.8)	7	1 (2)	14.3 (28.6)	20	6 (9)	30.0 (45.0)
Nov	18	6 (8)	33.3 (44.4)	7	1	14.3	25	7 (9)	28.0 (36.0)
Dec.	8	5	62.5	6	3	50.0	14	8	57.1
	252	79 (87)	31.3 (34.5)	148	24 (25)	16.2 (16.8)	400	103 (112)	25.7 (28.0)

[1] *Figures given in parentheses include isolations from larger amounts of powder (see text).*

In Table II is also shown the increase in positive samples due to the examination of the remaining 30 to 40 gm. of powder when the first examination proved negative. From September to December, 85 carlots were examined and *Salmonella* isolated from 36, nine of these or 25% being negative on the first test but positive in the larger sample. These increases made little difference in the order of incidence noted in Table I. Only one additional lot was found positive from the eastern plants (*E*). Four additional isolations were made from powder from Plant *I*, and two each from Plants *H* and *G*. These findings serve to emphasize the spotty distribution of these organisms in egg powder (6). It is also evident that, because of the small samples used in this investigation, the actual percentage incidence is higher than that reported here.

In the eastern plants, the percentage of carlots positive for *Salmonella* was greater in powders prepared from frozen egg than in those from shell or shell and frozen egg mixed (Table III). In one western plant (*H*) the percentage incidence increased when frozen egg was used, but in the others the type of egg used made little difference. In Plant *G* two of the four positive lots from shell egg were obtained with the larger samples of powder. If these are not considered there is little change in the percentage of positive samples from the different types of egg.

TABLE III

CARLOTS OF POWDER, CONTAINING *Salmonella* ORGANISMS, PRODUCED FROM SHELL EGGS, MIXTURES OF SHELL AND FROZEN EGG, AND FROZEN EGG

Plant	Shell			Shell and frozen			Frozen		
	No. carlots	No. positive	Percentage positive	No. carlots	No. positive	Percentage positive	No. carlots	No. positive	Percentage positive
Western									
A	4	1	25	1	—	—	8	2	25
B	16	3	18	33	5	15	13	3	23
G	10	4	40	4	1	25	21	4	19
H	13	2	15	38	8	21	28	14	50
I	22	14	63	30	21	70	7	5	71
K	—	—	—	—	—	—	4	—	—
	65	24	37	106	35	33	81	28	34
Eastern									
C	7	—	—	53	11	20	3	—	—
D	1	—	—	1	—	—	6	—	—
E	18	—	—	25	4	8	7	4	57
F	7	2	29	15	2	13	5	2	40
	33	2	6	94	17	18	21	6	29
Total	98	26	26	200	52	26	102	34	33

Fifteen types of *Salmonella* were found. These are listed in their order of incidence in Table IV. Most of the types found previously (6) were again encountered. *S. oranienburg* was the most common type, although 27 of the 45 strains were isolated from the powder produced by one plant. The three strains of *S. potsdam* were from the same plant (*H*) from which it was previously isolated (6). Of the new types, *S. montevideo* was found only in powder from eastern driers; eight of the nine isolations were from one drying plant. The strain of *S. paratyphi B* was tartrate positive; this is apparently a rare type in fowl. As far as can be determined, *S. selandia* has not been reported previously from fowl or eggs. It might be noted that one culture of *Aerobacter aerogenes* having antigens VI and VII was encountered from Plant *I*. Recently, several reports listing types of *Salmonella* isolated from dried egg have appeared elsewhere (14, 15, 18).

TABLE IV

TYPES OF *Salmonella* ISOLATED AND THEIR DISTRIBUTION

Type	No. of samples positive in:		Total
	252 western lots	148 eastern lots	
S. oranienburg	45	2	47
S. typhimurium	14	5	49
S. pullorum	12	5	17
S. thompson	9	5	14
S. montevideo	0	9	9
S. newington	7	1	8
S. bareilly	4	1	5
S. manhattan	4	—	4
S. potsdam	3	—	3
S. anatum	2	1	3
S. newport	—	1	1
S. paratyphi B	1	—	1
S. bredeney	1	—	1
S. tennessee	1	—	1
S. selandia	1	—	1
			134

In eight lots of powder two types of *Salmonella* were encountered. In all but one instance the types were of different groups since it was impossible to distinguish types in the same group with the sera available for the preliminary screening. The following pairs were obtained: *S. oranienburg* and *S. bareilly; S. oranienburg* and *S. newington; S. typhimurium* and *S. manhattan; S. typhimurium* and *S. bareilly; S. newington* and *S. bareilly*. *S. pullorum* was also encountered, along with *S. oranienburg* and with *S. bredeney*. All of the above were isolated from the product of one drier (*I*). *S. pullorum* and *S. typhimurium* were isolated from a sample from Plant *H*.

Of the 17 strains of *S. pullorum* isolated, 14 were found only on bismuth sulphite agar plates. The superiority of this medium over SS agar for *S. pullorum* was also noted in isolations from chicks. This has recently been reported by others (16). Schneider (15) claims that selenite F enrichment is superior to tetrathionate broth for the isolation of *S. pullorum*, although it is not stated whether equally good results were obtained with both the SS and desoxycholate citrate agars used. In the present study, of 51 isolations of types other than *S. pullorum*, 36 were isolated on both media, nine from SS agar only, and six from bismuth sulphite agar only. When organisms of the same group were found on both media it was assumed they were of the same type.

Of the 17 strains of *S. pullorum* isolated, 12 were checked for the 'X' variant (2, 19) by means of partially absorbed sera. Three were classed as the variant, five as intermediates, and four as the normal strain.

Estimates of the most probable number of *Salmonella* present were made on 54 lots. During most of the period, estimates were made only on samples in which three or four of the quadruplicate lots were positive. Of the 54 samples checked, in all but four the M.P.N. was less than one per gram. In four samples the M.P.N. was 1.3, 2, 3, and 9.4 per gram.

During June and July, samples from 12 carlots of dried sugar–egg powder from Plant *F*, six from Plant *A*, and three from Plant *B* were examined. *S. pullorum* was isolated from one lot from Plant *A*. No other *Salmonella* types were encountered in this product.

Source of *Salmonella* Infection

There is a growing literature to support the suggestion made previously (6) that in hens' eggs the *Salmonella* organisms, other than *S. pullorum*, come from fecal contamination on the shells, as has been noted by many authors with other types of fowl. Watt (17) isolated *S. montevideo* from the meats of eggs responsible for an outbreak, and in an examination of over 5000 hen eggs recovered *S. cholerasuis* and *S. derby* from a few. He apparently did not find *Salmonella* on the shells. Although the evidence was not very definite, the outbreak reported by Crowe (5) was probably due to infected meats. On the other hand, it has been shown that the shells of eggs laid by hens carrying *Salmonella* organisms are at times contaminated with these organisms (8). Gordon and Buxton (10) also indicate that in an outbreak in a hatchery the organisms were probably carried by fecal contamination. Chase and Wright (4) failed to isolate any *Salmonella* types, other than *S. pullorum*, from the meats of 2000 and the exterior of 400 eggs. A recent contribution (16) gives ample evidence that more dirty eggs carry *Salmonella* organisms than do clean eggs. Our attempts to trace the source of these organisms are reported below.

From November, 1944, to August, 1946, eggs were received from six points across Canada at monthly intervals for another study (13). Five dozen each of Grades *A* large, *A* medium, *A* pullet, *B*, and *C* were received each time and broken out for drying. The shells of each lot were collected in sterile beakers, packed loosely, and covered with tetrathionate broth. In all, the shells of 195 lots or 975 dozen eggs were examined. Samples (approximately 100 ml.) of the broken out egg were also examined. *S. pullorum* was isolated from two samples of melange and one lot of shell. No other *Salmonella* organisms were encountered.

In addition, the shells and contents of some 48 dozen other eggs of various grades have been examined with negative results. This represents a total of 12,276 eggs from various parts of Canada. However, this is a very small sample when it is considered that between 120,000 and 180,000 dozen eggs go into one carlot of powder.

In an infected flock one might expect different results. When a number of chicks from a Saskatchewan hatchery were found to be infected with *S. bareilly*, the eggs from which the chicks were hatched were traced back to two farms, and in May, 1945, a dozen eggs from each flock was obtained. Both shells and egg meats were examined by a technique already described (9). The untreated egg is placed between ring clamps, which are kept painted with tincture of iodine, and the meat is removed as previously indicated. The shell is then broken up using two pairs of flamed forceps and put into tetrathionate broth. The small amounts of iodine carried over are neutralized by the excess thiosulphate in the broth. *S. bareilly* was isolated from the shells of two of the eggs from one farm (*L*) and of six of the eggs from the other (*M*). No organisms were found in the meats. In August six dozen eggs were obtained from each of these farms. All from one lot (*L*) were negative, but *S. newington* was found in the meats of two eggs from the other farm (*M*). No *Salmonella* organisms were recovered from the shells of these eggs.

In Plant *I* in May, 1946, the shell and contents of 40 dirty eggs were examined as well as swabs of the shells of 89 dirty eggs. No *Salmonella* was obtained. Samples of melange, shell drip, etc., were taken at various times but only one isolation was made; *S. pullorum* was found on an emulsifier screen. Three samples collected on one day in July from the by-pass to the high pressure pump and one from the holding vat were positive for *S. oranienburg*.

At Plant *H*, 52 dirty eggs were examined, with negative results. Five lots of shells from at least three dozen eggs each were collected at the breaking tables and cultured but no *Salmonella* was found. However, *Salmonella* types (*S. bareilly*, *S. oranienburg*, and *S. thompson*) were recovered in 7 out of 12 samples of the albumen draining from the barrels of egg shells. During the same period, isolations were made from 4 of 20 samples of melange taken at various points in the plant (*S. potsdam*, *S. bareilly*, *S. thompson*). It cannot be said whether these organisms came from the inside or outside of the eggs, although the greater incidence in the shell drippings would point to the latter.

It would seem therefore that where flocks are known to be carriers or if large enough samples of commercial eggs are examined, *Salmonella* organisms may be recovered from the eggs. The evidence presented is still insufficient to say that it is due solely to fecal contamination.

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QUANTITATIVE STUDY OF THE HILSCH HEAT SEPARATOR[1]

By A. F. Johnson[2]

Abstract

The 'heat separator' is a very simple device for attaining a temperature drop of the order of 30 centigrade degrees by means of a stream of air. An air jet enters a long cylindrical chamber near one end, and is directed so as to maintain a high velocity vortex. Air drawn off from the centre of the vortex is cooled, while the remainder, flowing down the length of the chamber, is warmed. The present paper describes results of a quantitative study of the performance of the device. Although the maximum efficiency is only about 15%, as compared with an ideal adiabatic expansion of the total flow, it provides a practical means of cooling for many purposes.

Introduction

The apparatus described in this paper as a 'heat separator' is a simple device for producing cold by the separation of a high velocity gas vortex into cold and warm streams. Compressed air enters a long cylindrical chamber through a tangential nozzle near one end. If that end of the cylinder is closed by a diaphragm that permits the escape of the gas only from the central region, while the other end is throttled, the gas escaping through the central diaphragm is cooled, while the gas escaping through the other end is warmed. With our apparatus, temperature differences in excess of 40 centigrade degrees have been obtained between the inlet and the cooled gas stream.

The device was introduced to this continent by R. M. Milton, who described it informally at a meeting of the American Chemical Society in April 1946 (2). He had obtained it from Hilsch's laboratory in Erlangen. No data on its performance were available, and, since it seemed probable that it would have useful applications, the present quantitative study was undertaken. Since the submission of the present paper, a paper by Hilsch (1) has appeared. The results of the present investigation are in substantial agreement with those reported by Hilsch and are given below in summary only.

The apparatus (Fig. 1) consists of a cylindrical block, B, of lucite containing a central cylindrical chamber, C. Air under pressure enters this chamber tangentially through the fine orifice, A (0.047 in. in diameter). The entering stream is guided into a spiral flow, with a high angular velocity, by a C-shaped eccentric ring, which is shown at E, and at xy in the cross section, $I-I'$. The chamber is extended to the right by means of a German silver tube, T_1, whose internal radius is equal to that of the eccentric at y. On the left is a small orifice, O, on the axis of the chamber leading to another tube, T_2. The fitting F_2 projects into the chamber so that the opening of the orifice O is in the plane of the near side of the eccentric.

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[1] *Manuscript received in original form December 27, 1946, and as revised, June 20, 1947. Contribution from the Department of Physics, University of Toronto, Toronto, Ont.*

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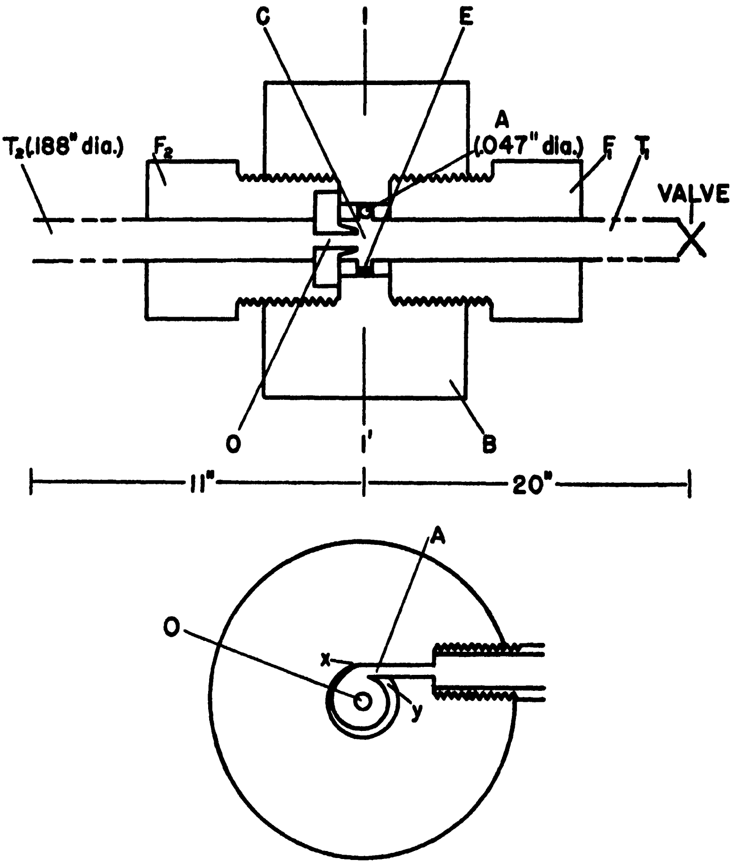

SECTION I-I'

Fig. 1. *Cross section of heat separator.*

Gas is supplied at pressures from 30 to 200 p.s.i. (gauge), and escapes into the vortex chamber with a high tangential velocity. That portion of the gas that escapes through the small orifice (that is, from the centre of the vortex) is cooled, and that which escapes through the other end is warmed. The corresponding tubes will be referred to as the cold and warm ends respectively. The valve on the warm end is approximately 20 in. from the centre of the block, and controls the ratio of the flows through the two ends.

Measurements

The dimensions of the apparatus used for these measurements are approximately the same as those of the smallest size described by Hilsch. The temperatures of the two gas streams were measured by thermocouples at the following points: soldered to the warm tube near the valve; inserted into the cold end so that the junction was close to the outer end of the orifice. The other junctions of both thermocouples were soldered to the inlet pipe near the block, *B*. These thermocouples could be read to a precision of 0.3° to 0.1° C. depending on the series resistance used.

In order to test the assumption, upon which Hilsch (1) has expressed doubt, that thermocouples so placed measure the temperatures of the gas streams, the enthalpy was calculated in selected cases. For example, with an input pressure of 90 p.s.i., input temperature of 17.2° C., and flow ratio (warm end flow to cold end flow) of 5.12, the warm and cold outlet temperatures were 23.3° C. and −19.8° C. respectively. With these data, the sum of the enthalpies of the exit streams agrees with that of the input within one per cent.

In order to determine the optimum working conditions, three variables were studied: input pressure, ratio of flows, and diameter of the orifice, *O*.

Using an orifice of 0.064 in. diameter, a series of measurements was made varying input pressure and flow ratio. These are in general agreement with graphs given by Hilsch. The maximum temperature drop observed was 42.8 centigrade degrees with input pressure, 200 p.s.i. and flow ratio, 4.3. However, this maximum temperature drop is obtained at the expense of a very low efficiency.

It is more significant to consider (i) the product of the temperature drop and the fraction of flow out the cold end, described below as 'useful cooling'; (ii) the ratio of the useful cooling to the theoretical adiabatic temperature drop at the same input pressure. The latter gives an indication of the efficiency as compared with an ideal expansion engine. The maximum useful cooling with this orifice was 10.6 centigrade degrees and the maximum efficiency was .071.

The graphs published by Hilsch indicate that the temperature drop at the cold end disappeared when the warm end flow was reduced to zero. In the author's experiments a cooling of 5.5 degrees was found when the warm end was closed, with an input pressure of 100 p.s.i. It is of interest that this cooling is definitely greater than that which the Joule–Thomson effect alone would produce, which for the above conditions is calculated to be 1.7 degrees.

Results of varying the diameter of the orifice, *O*, are also in general agreement with those of Hilsch. An orifice of 0.107 in. diameter was found to be the optimum in respect to both temperature drop and efficiency. This gave an optimum working condition at 100 p.s.i. as follows: flow ratio, 0.38; temperature drop, 24.8 degrees; useful cooling, 18.0 degrees; and efficiency, 0.14.

Samples of air taken from the two ends were analysed and the results gave no indication of any separation of the air into its components in passing through the heat separator.

A few measurements were made with carbon dioxide and hydrogen in place of air. For these gases a cold end orifice of 0.094 in. diameter was used, and the input pressure was kept constant at 100 p.s.i. These measurements are summarized in the table below. The setting of the warm end valve was such as to give a flow ratio with air of 0.61. It was not possible to measure directly, with the rotameters available, the flow ratio for hydrogen. The figures for useful cooling and efficiency in this case are based on the assumption that the flow ratio is the same as that for air. The total flow through the apparatus is given in litres per minute at 1 atm. and 21° C. In the last column the product, Q_r, of the mass flow per minute through the cold end, the specific heat, and the temperature drop is given for each case. This product is a measure in calories per minute of the heat removed from the gas flowing out the cold end.

	Temperature drop, centigrade degrees	Useful cooling, centigrade degrees	Efficiency	Total flow, litres/min.	Q_r calories per minute
Air	19.5	12.1	.093	95	352
CO_2	19.8	12.3	.095	67	329
H_2	15.9	9.9	.076	430	1320

Possible Uses

It seems unlikely that the heat separator will replace any of the standard methods of refrigeration or gas liquefaction. It is less efficient than an expansion engine for liquefiers of the Claude type. Although it is more efficient than the Joule–Thomson effect for a liquefier of the Hampson type, the problem of removing the warm end flow without affecting the performance of the heat exchangers may make it impracticable. However, it is a simple and inexpensive device and can be a useful refrigerating agent for laboratory and other purposes where compressed air supplies are available and where more elaborate refrigeration machinery might not be economical.

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THE DYEING OF NATURAL COTTON WITH DIRECT DYES: A DETERMINATION OF THE HEAT OF DYEING[1]

By R. P. Graham[2] and H. J. Fromm[3]

Abstract

The equilibrium sorption of a purified direct dye on natural cotton yarn has been determined over a range of dye-bath concentrations (20 to 175 mgm. of dye per litre of solution) and temperatures (75° to 90° C.). The liquor-to-yarn ratio in the dye bath, which contained sodium chloride (4.00 gm. per litre), was sufficiently high to permit the concentration of dye in solution to remain essentially constant throughout a dyeing experiment. The dye was removed from the skeins using a pyridine–ethanol–water solution, and the concentration of dye in the latter determined spectrophotometrically.

Differential heats of dyeing may be calculated from the results obtained. For an equilibrium sorption of 475 mgm. of Calcodur Blue 4GL per 100 gm. of natural cotton yarn, the value of 15 kgm-cal. per mole was found, and it is shown that the differential heat of dyeing increases as the value of the equilibrium sorption decreases. The results are interpreted in the light of the modern view of the structure of cellulose.

Introduction

In a relatively recent publication from this laboratory (7) reporting a study of the dyeing of natural cotton with direct dyes, reference was made to review papers dealing with the dyeing of cellulose with direct dyes and to other recent papers concerned with this subject, and, in particular, the interaction of direct dyes and cotton. Since this earlier paper was written, a number of significant contributions to our knowledge of the direct dyeing of cellulosic materials have appeared. Of these there may be mentioned the discussion of the physical chemistry of dyeing by Valko (28, pp. 594-619), the paper by Standing, Warwicker, and Willis (25) in which the direct dyeing process is assumed to be essentially one of diffusion in the cellulose and in which a diffusion–adsorption equation is developed and its validity tested by applying it to experimental data published by Neale and his collaborators; the paper by Morton (12) in which a molecular theory of the dyeing of cellulose with substantive dyes is presented; and that by Lemin, Vickers, and Vickerstaff

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(9) (a paper that gave rise to published discussion (1, 29)) in which the results of a study of the rate of dyeing of numerous direct dyes, including binary combinations, on cotton are presented as well as other studies leading to a proposed classification of direct dyes from the point of view of practical application. The report of the committee appointed in 1944 by the Council of the Society of Dyers and Colourists to discuss the dyeing properties of direct cotton dyes was published some months ago (5). Other recent papers concerned with the interaction of direct dyes and cellulose are those by Rose (22), Neale (14), Brass and Schreier (3), and Wälchli (30).

Direct cotton dyes have been known for over sixty years (31), but our understanding of their action is still very inadequate. In the last 15 years an appreciable number of careful studies of the dyeing of cellulosic materials by direct dyes have been carried out, but to date very little attention appears to have been given to the energetics of the process. The authors are aware of only two published determinations of the heat of dyeing of direct dyes on cellulose (11, p. 274; 32); both of these determinations were made using viscose sheet. In the present investigation a number of isotherms for the sorption of a purified blue direct dye on natural cotton yarn were determined. From these data, values for the heat of dyeing have been calculated and an attempt has been made to interpret their variation with the extent of equilibrium sorption.

Materials and Methods

Cotton

Natural cotton yarn from the same batch as that used in an earlier study (7) was the sorbent; the yarn was 1/4's count wound in 14 oz. packages on Franklin springs.

The cotton was wound by hand into small skeins (weighing slightly more than 0.2 gm.) and then dried, weighed, etc., by the procedure described before (7) to give a skein weighing, in the present study, 0.2000 ± 0.0005 gm. on a dry basis. Before being dyed, the weighed dry skein was allowed to stand in air for some hours.

Dyestuff

The trisazo direct dye Calcodur Blue 4GL (Colour Index 533), after purification, was used throughout the present study. The method of purification, based on that recommended by Rose (21), was a slight modification of that used in the earlier study (7). The essential differences were that the precipitate produced by the interaction of the dye with di-*o*-tolylguanidine was washed with a very dilute solution of di-*o*-tolylguanidine hydrochloride rather than with distilled water (to decrease the tendency of the precipitate toward peptization); that the regenerated dye was washed with isopropanol (99%) rather than with methanol; and that before use the ground dye was dried for 24 hr. *in vacuo* at 110° C. over phosphorus pentoxide—this procedure served to remove residual di-*o*-tolylguanidine from the dyestuff.

Dyeing Apparatus

The dye pots consisted of short-necked round-bottomed Pyrex boiling flasks of three litres' capacity to which were attached, by means of a rubber stopper, water-cooled condensers. The cotton yarn to be dyed was attached to a Pyrex glass skein holder (loosely, by means of platinum wires), which also served as a stirrer. The glass shaft of the stirrer passed up through the condenser and was given an up-and-down motion (two cycles per second) by an electromagnetic device similar in principle to the one described by Tulk and Seagers (26) but with the following modification, which resulted in more uniform operation: the pendulum was removed and there was substituted a wooden wheel (driven by a constant speed induction motor) carrying a semicircular phosphor bronze strip. Two fixed phosphor bronze brushes, which were in series with the electromagnetic stirring motors, pressed on this strip; thus, as the wheel revolved, the circuit was alternately closed and opened in very regular cycles.

The dye pots were immersed in a constant temperature bath constructed so as to permit a temperature control of ± 0.1° C. in the range 70° to 97° C. Temperatures reported in this paper are corrected for exposed stem, and were determined using a thermometer that had been compared with one newly calibrated in the Division of Physics of the National Research Council of Canada.

Dyeing Procedure

In all dyeing experiments reported in this paper, 0.2000 ± 0.0005 gm. (dry weight) of natural cotton yarn was dyed using 2900 ml. of dye-bath solution containing 4.00 gm. per litre of sodium chloride (analyzed grade); the liquor-to-yarn ratio was thus 14,500 : 1. The dye bath contained dye at a concentration ranging from 20 to 176 mgm. per litre (2.3×10^{-5} to 2.0×10^{-4} *M*). These conditions, which are of course far removed from those used in commercial dyeing, permitted equilibrium dyeing to be attained at the temperatures employed in a reasonable length of time (12 to 48 hr.) without any significant change occurring in the concentration of dye in the dye bath (in all experiments, the exhaustion at equilibrium was less than 1.1%).

The dye solution was placed in a dye pot, which, with condenser attached, was preheated over a burner and then was immersed in the thermostat for a period of one hour (to permit thermal equilibrium to be established) before the cotton skein and stirrer were inserted and the dyeing experiment begun. Dyeing was allowed to proceed, under constant temperature conditions, for an appropriate length of time (which, in all experiments except those concerned with rate of dyeing, was until equilibrium sorption had been attained) and then the skein was removed from the dyeing apparatus; it was squeezed dry, rinsed twice in 0.4% sodium chloride solution, again squeezed dry by hand, and then placed in the stripping apparatus (*vide infra*) for removal of the dye. Each rinsing solution consisted of 100 ml. of the sodium chloride solution. No color could be detected visually after rinsing. Because a concentration of this dye as low as 0.05 mgm. per litre can be detected visually, there was less than 0.01 mgm. of dye removed in the rinsing operation (which was designed to eliminate entrained dye liquor). On the other hand, analysis showed the 0.2 gm. cotton skeins to contain from 0.39 to 1.00 mgm. of dye.

The used dye-bath solution was filtered through a fritted glass disk in order to ascertain whether any appreciable amount of cotton had become separated from the skein. If such was the case, the run was discarded; this occurred in about 5% of the experiments.

Analytical Procedures

A number of workers (e.g., 2, 3, 9, 15) have used pyridine (usually 15 to 25% aqueous) to remove direct dyes from cellulosic material prior to colorimetric determination; this stripping technique was developed from some observations made by Ratelade and Chetvergov (19). Investigations in this laboratory have shown that, at least in the cases of Calcodur Blue 4GL, a solution consisting (by volume) of 25% pyridine (reagent grade), 10% ethanol (95%), and 65% distilled water permitted a significantly faster rate

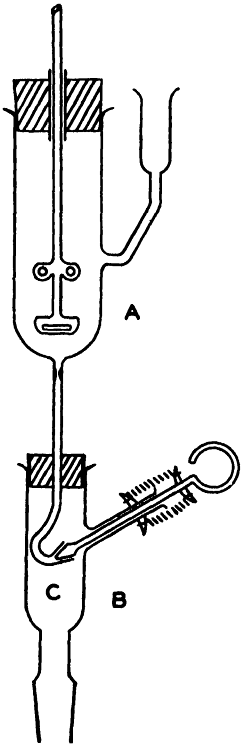

FIG. 1. *Apparatus for removing dyestuff from the dyed skein.*

of dye stripping (at room temperature) than did a 25% pyridine in water solution and, moreover, spectrophotometric tests showed the dye was more stable in the pyridine–ethanol–water solution than in one without alcohol.

The dyed skeins were stripped using the apparatus shown in Fig. 1. The dyed cotton skein was attached (loosely, by means of platinum wires) to the stirrer in the upper chamber. After closing the plunger-operated ground-glass joint at *C*, sufficient stripping solution was introduced through the side arm at *A* to cover the cotton skein, and the stirrer carrying the latter was rotated by an electric stirring motor (not shown). At the end of one hour, the solution was drained from the skein by opening the joint at *C* and allowing the solution to drain through chamber *B* into a 250 ml. volumetric flask (not shown) connected to *B* by a ground glass connection. Fresh stripping solution was introduced, stripping allowed to continue for a further period of six hours, the solution drained again, and a third stripping action allowed to continue for 16 hr., or overnight. The cotton was then rinsed with the stripping solution and the liquid in the volumetric flask made up to volume with the stripping solution. All stripping operations were carried out at room temperature.

A portion of the dye solution from the volumetric flask was placed in a cuvette and the transmittance of the solution measured, at 600 mμ, using a Coleman Model 11 Universal Spectrophotometer fitted with the 'PC-4' filter. Matched rectangular cuvettes, with a path length of 10 mm. were employed; the reference cuvette contained pure stripping solution. From the measured transmittance, the amount of dye originally on the fibre could be calculated, making use of a calibration curve (Fig. 2) constructed from data obtained using solutions of known concentration of dye dissolved in the pyridine–ethanol–water stripping medium.

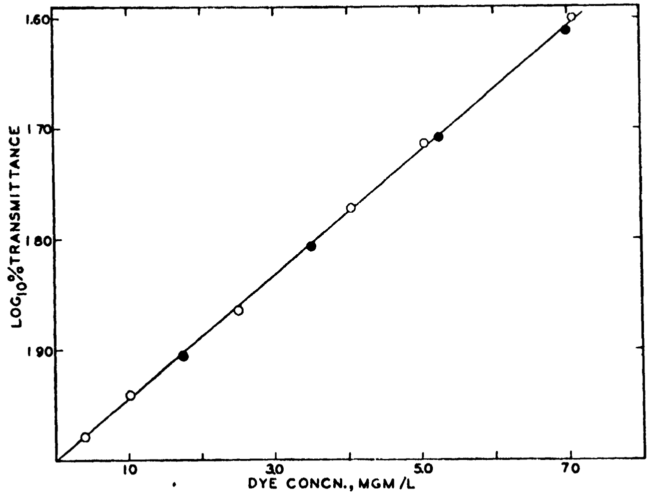

FIG. 2. *Calibration curve (two separate determinations) for the colorimetric determination of dye using the spectrophotometer at a wave length setting of 600 mμ.*

Experimental Results

Rate of Dyeing

A number of rate of dyeing experiments were carried out in order to ascertain the time required to reach equilibrium sorption under the conditions being used to obtain the sorption isothermal data reported below. Examples of the type of rate curves obtained are shown in Fig. 3. This and other related data, together with the knowledge that the time required to reach equilibrium decreases (at constant temperature) as the concentration of dye in the dye bath decreases, and decreases (at constant dye-bath concentration) as the temperature increases (7), permitted the choice, in the sorption experiments hereinafter described, of dyeing times sufficiently long to have ensured the establishment of equilibrium conditions.

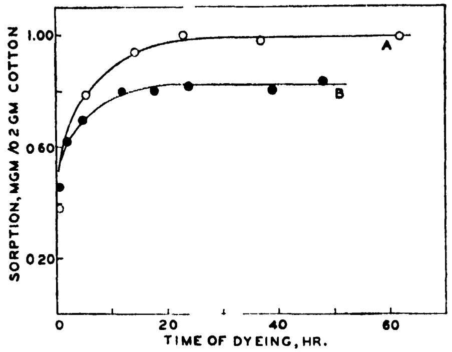

FIG. 3. *Typical rate of sorption curves. Both are for dyeings at 90° C.; the concentration of dye in the bath in Curve A was 200 mgm. per litre of solution, and in Curve B it was 100 mgm. per litre.*

Sorption Isotherms

Three sorption isotherms, at the temperatures 74.4°, 82.4°, and 89.3° C. were determined using the techniques described above. One of these isotherms is shown in Fig. 4, and all three are shown on a log–log plot in Fig. 5. Since the extent of the exhaustion of the dye bath is negligible (less than 1.1% in all cases) the abscissa is the logarithm of either the initial or the equilibrium dye concentration. The experimental data used to construct these curves are given in Table I.

Heat of Sorption (or Dyeing)

If we consider the reaction illustrated by the equation: cellulose-dye sorption complex = cellulose + dye (in solution), and note that the sorbed dye represents a condensed phase of the dye, we may with some justification apply to the system the equation:

$$\frac{d\ln C}{dT} = \frac{\Delta H_d}{RT^2} \text{ or } \frac{d\ln C}{d(1/T)} = -\frac{\Delta H_d}{R}$$

where T, the temperature, is in degrees absolute, C is the equilibrium concentration of dye in solution, ΔH_d is the heat absorbed in the transition from one phase to another (in this case, desorption) in calories per mole of dye if R, the gas constant, is expressed in calories per mole.

If, then, ΔH_d may be assumed to be independent of temperature (and such may be expected over a small temperature range) a plot of $\log_{10}C$ (for a fixed value of sorption) against $1/T$ should yield a straight line, the slope of which is $-\dfrac{\Delta H_d}{2.303\,R}$. Such plots, for various values of the sorption, are shown in Fig. 6, which was constructed from data obtained using Fig. 5. The slopes of the lines are negative, which means that ΔH_d is positive (or heat is absorbed) in the desorption reaction; the sorption reaction is exothermic.

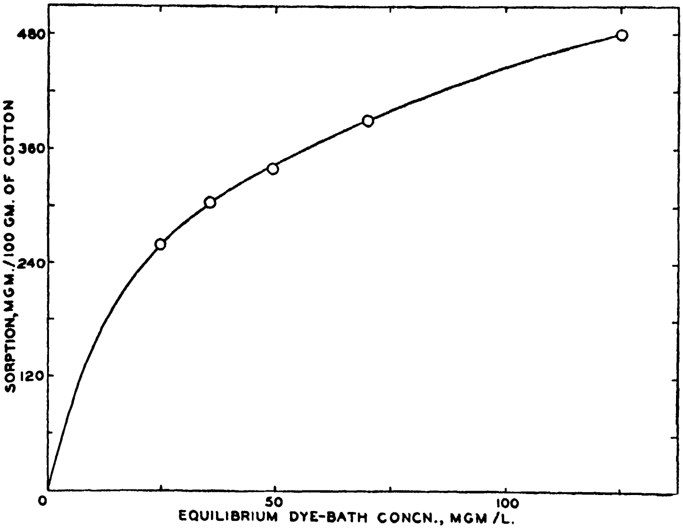

FIG. 4. *Sorption isotherm for a dyeing at 82.4° C.*

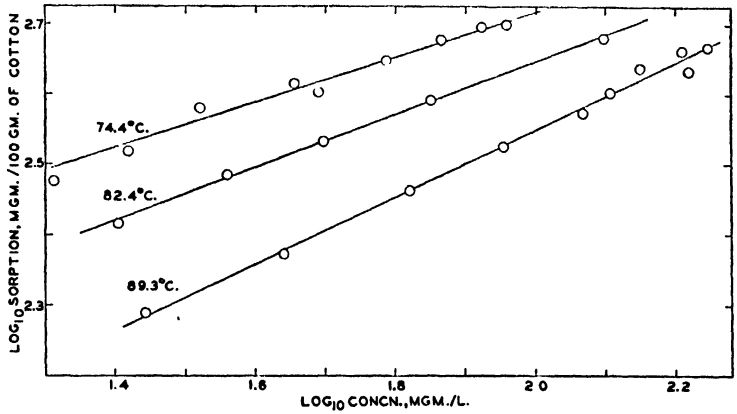

FIG. 5. *Log–log plots of sorption isotherms.*

The values for the heats of sorption (or dyeing) calculated by this method are given in Table II. The heat of dyeing is $-\Delta H_s$, which is equal to ΔH_d.

TABLE I

EQUILIBRIUM SORPTION AS A FUNCTION OF TEMPERATURE AND CONCENTRATION OF DYE IN THE DYE BATH

Temperature of dyeing, ° C.	Concentration of dye in the bath, mgm./litre	Dye sorbed on the cotton, mgm./100 gm.
89.3	27.8	195
	43.6	235
	66.0	290
	90.0	335
	116.6	375
	127.9	400
	141.2	435
	162.3	460
	165.5	430
	176.6	465
82.4	25.3	260
	36.1	305
	49.8	340
	70.8	390
	125.4	480
74.4	20.5	300
	26.2	330
	33.2	380
	45.2	410
	49.0	400
	61.1	445
	73.3	475
	83.6	495
	90.6	500
67.4	25.2	380
	25.3	385

TABLE II

HEAT OF DYEING AT VARIOUS VALUES OF EQUILIBRIUM SORPTION

Sorption, mgm. dye per 100 gm. cotton	Heat of dyeing ($-\Delta H_s$), kgm-cal. per mole of dye sorbed
473	15.2
422	17.1
383	18.8
355	20.3
316	22.4

Effect of Temperature on Sorption

The data of Table I, and the graphs drawn in Fig. 5 using these data, permit the drawing of some curves illustrating the relation between the amount of dye sorbed at equilibrium and the temperature of dyeing, under conditions of constant concentration of dye and sodium chloride in the dye bath. These curves are shown in Fig. 7.

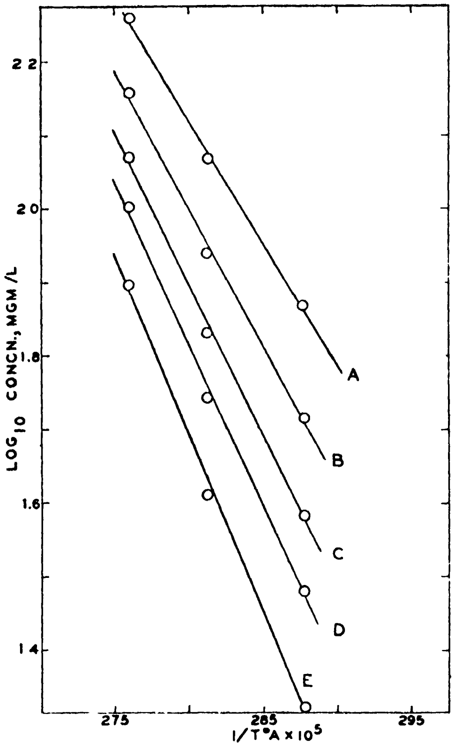

FIG. 6. *'Isosteric' plot relating the equilibrium concentration of dye in the bath to the temperature, at constant values of the equilibrium sorption. The sorption values, in mgm. of dye per 100 gm. of yarn, are: Curve A, 473; Curve B, 422; Curve C, 383; Curve D, 355; Curve E, 316.*

Discussion

The rate of dyeing curves (Fig. 3) are of the type to be expected, and it is not surprising that the sorption isotherms (data of Table I) may be fitted by a Freundlich type equation, as is evidenced by the linearity of the log–log plot in Fig. 5. (The data will not, incidentally, fit the Langmuir sorption isotherm equation.) It may be noted that the forms of the rate of sorption curves and of the sorption isotherms obtained in the present experiments where the exhaustion of the dye bath at equilibrium varied from 0.2 to 1.1% are the same as those obtained in earlier work (7) using the same dye and sorbent, but under conditions such that the dye-bath exhaustion was over 90%.

It should be pointed out that the lines in Fig. 5 are not parallel; the slopes vary from 0.32 at a temperature of 74.4° C. to 0.47 at 89.3° C. The value of the equilibrium sorption always increases with increasing residual dye-bath concentration, but the degree of increase decreases as the temperature decreases. This same effect can be seen in the data of Willis *et al.* (32) for the sorption of Chrysophenine G on viscose sheet in the plot of the isotherms they obtained under conditions, as in the present work, of a fixed concentration of sodium chloride.

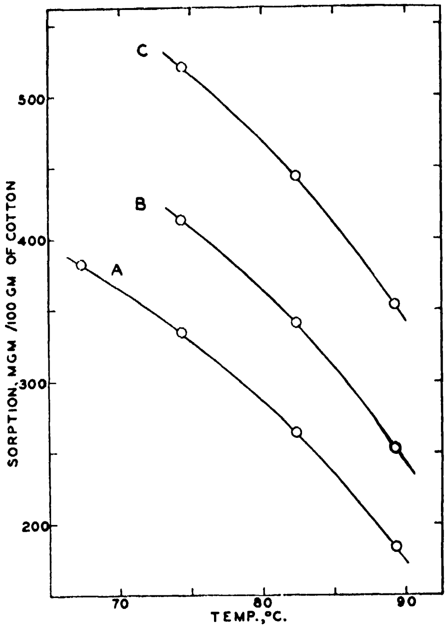

FIG. 7. *'Isobaric' plot relating the equilibrium sorption of dye to the temperature, at constant values for the equilibrium concentration of dye in the bath. The dye-bath concentrations, in mgm. of dye per litre of solution, are: Curve A, 25.2; Curve B, 50.1; Curve C, 100.0.*

It will be noted that the best line drawn through the points in Fig. 6 would show a very slight curvature, rather than being linear as drawn. The slight curvature (if real) may be due to a possible change in the structure of the cotton with changing temperature. It has been pointed out (24) that this consideration requires that care be exercised in deducing the heat of dyeing from the temperature coefficient of the equilibrium sorption. It should also be borne in mind in work of the present type that the sorption values recorded include the mass of any dye that may be present in entrained dye liquor.

The heat of sorption or heat of dyeing values determined by the method yielding the values recorded in Table II are differential heats of sorption (4, p. 26; 10, p. 400), and it is evident that the values increase significantly as the extent of equilibrium sorption decreases. A consideration of the structure of cellulose is helpful in seeking an interpretation of this phenomenon.

It is generally considered that cellulose fibres are composed of crystallites in which the cellulose chains are closely packed together with amorphous intercrystalline regions where the packing of the chains is less regular and their orientation is irregular (17; 23, pp. 203-252; 24). 'Amorphous' is not used here in the sense of a complete lack of geometrical order, but rather to indicate matter that causes a general fogging in the X-ray diagram rather than giving rise to definite diffraction lines. Experiments have indicated that when water molecules are sorbed by cellulose they are able to penetrate the intercrystalline or intermicellar regions, but they are not able to penetrate the crystallites (24; 27, pp. 412-414; 28, pp. 595-596); there is direct evidence that in the sorption of direct dyes by cellulose, the dyes, likewise, do not enter the crystallized regions (28, p. 612). It is to be expected that because cellulose is not homogeneous, its sorption affinity for a particular dye will not be uniform over all the surface with which the dye may come into contact. It is reasonable to suppose that the heats of sorption associated with the different portions of the surface will vary, and, moreover, that the most active (in the sense of sorption affinity for the dye) portions of the surface will be the first to be covered with dye.* This interpretation accounts, qualitatively, for the results found in this work, i.e., that the higher values of the heat of dyeing (or sorption) are associated with the lower values of the equilibrium sorption. (There may also occur multilayer dye sorption where the energy released in the sorbate–sorbate interactions is less than that released, in the earlier stages of sorption, due to sorbate–sorbent interactions.) A variation of the heat of sorption with the amount of sorption is commonly encountered in the study of the sorption of gases and vapors on solids (4, pp. 215-229, 246-253; 10, pp. 405-422). In such systems, ordinarily (although not always (4, pp. 251-262; 8)) the differential heats of sorption decrease with increasing amounts of gas sorbed (4, pp. 26, 247); this variation in the heat of sorption is generally attributed to interactions between sorbed particles, or to nonuniformity of the surface of the sorbent as a result of the surface atoms being separated by varying distances or arranged in differing geometrical configurations (which lead to different interaction energies with the same sorbate molecule) or to the presence of crevices, pockets, etc., in which the heats of sorption are different from those on a plane surface (4, pp. 261-262).

Calculations using the data of Willis *et al.* (32), who studied the sorption of a direct dye on viscose sheet, show that the heat of dyeing decreased with decreasing concentration of sodium chloride in the dye bath (for a given value of the equilibrium sorption), and, as was found in the present work, that the heat of dyeing decreased with increasing values of the equilibrium sorption (for a constant value of the sodium chloride concentration). Using Chrysophenine G (Colour Index 365), Willis *et al.* (32) found values of the heat of dyeing varying from 9.3 to 15.9 kgm-cal. per mole. Meyer has calculated

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* *In this connection it is interesting to note that in stripping experiments it was found that most of the dye was removed in two hours, but that over 20 hr. was required to reduce the dye left in the skeins to a trace. Many additional hours of stripping action failed to remove the last trace of dye; this portion was evidently very strongly bonded to the cotton.*

(11, p. 274), from data of Garvie, Griffiths, and Neale (6) a value of 5 kgm-cal. per mole for the heat of dyeing in the case of Chlorazol Fast Red K (Colour Index 278) on viscose sheet, but the present authors do not accept this value. We are not satisfied that the data available permit a calculation of the heat of dyeing in this case. These and other workers have postulated that the sorption of direct dyes on cellulose is due to hydrogen bond formation, and have suggested that the values found for the heat of dyeing lend support to this view. The present authors do not feel that values for the heat of dyeing can, *per se*, be of much, if any, help in supporting the hydrogen bonding theory because of the complexity of the situation: one cannot consider that the average direct dye is necessarily bound to the cellulose by only one hydrogen bond,* and even if this were possible, the energy associated with the formation of a hydrogen bond is, according to Pauling (18, p. 333), in general from 4 to 8 kgm-cal. per mole depending upon the atoms bonded and on the substance in which the bonding occurs. The hydrogen bond is thus a relatively weak bond (18, p. 284; 20, p. 146). Valko has pointed out (28, pp. 606-607) that although hydrogen bonding may well be an important factor in accounting for the interaction between dye and fibre, there are other types of forces to be considered.

It has been stated (24) that the temperature coefficient of the equilibrium sorption depends (although to a small extent) on the dye, the cellulose, and the salt concentration. In studying the sorption of direct dyes on viscose, Neale found that the equilibrium sorption is roughly halved by a rise in temperature of 20° C. (16) or (a later figure) 30° C. (13). In the present work it was found (Fig. 7) that at a constant dye concentration of 25 mgm. per litre the equilibrium sorption of Calcodur Blue 4GL on natural cotton yarn was approximately halved by a rise in temperature of 20° C., from 70° C. to 90° C., but that as the equilibrium dye concentration in the bath increases (at a fixed salt concentration) a greater temperature range is required in order to effect a halving of the equilibrium sorption. The temperature coefficient of the equilibrium sorption thus depends on the equilibrium concentration of dye in the bath, which statement is, of course, deducible from the finding that the value of the differential heat of sorption depends on the extent of the equilibrium sorption.

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* *With a given dye, spatial considerations may require that certain of the dye particles arriving at the surface after a measure of sorption has taken place form fewer bonds than do those arriving earlier at the fresh surface.*

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THE OCCURRENCE AND DISTRIBUTION OF *SALMONELLA* TYPES IN FOWL

II. STUDIES OF ARTIFICIAL *S. BAREILLY* AND *S. ORANIENBURG* INFECTIONS IN HENS[1]

By F. E. Chase[2]

Abstract

Experimental studies carried out on a limited number of hens infected orally with *S. bareilly* indicated that occasionally such hens may lay contaminated eggs. Using the estimated numbers of *S. bareilly* in the feces as the criterion of infection, considerable variation in susceptibility was evident, the carrier period ranging from 5 to 40 days. The organisms were recovered from the intestinal tract and in one instance from the spleen. The apparent development of resistance to repeated oral inoculation was demonstrated. Experiments of a similar nature were made with hens infected orally with *S. oranienburg*. No contaminated eggs were found, though in this case low egg production resulting from some of the hens moulting reduces the significance of this finding. Fecal counts were lower than those obtained from the *S. bareilly* infected hens. *S. bonariensis* was isolated from the feces of two hens during this experiment.

Introduction

The isolation of *Salmonella* types from Canadian dried egg powder by Gibbons and Moore (6) has served to stimulate interest in the probable source of these contaminants. There is ample evidence in the literature to show that chickens and hens may act as host to many *Salmonella* types in addition to the long recognized *S. pullorum* (9, 10), and in the case of closely related fowl, such as ducks, pigeons, and turkeys, that contaminated eggs may be produced by birds naturally infected with *Salmonella* organisms (3, 8).* It has also been demonstrated by Shalm (11) that the contents of hens' eggs may become contaminated with *Salmonella* as a result of smearing the unbroken shells with contaminated feces.

However, the expected isolation of *Salmonella* types, other than *S. pullorum* from hens' eggs, has been slow in appearing (2),** but it has been reported recently by Watt (12) in his account of a food poisoning outbreak that occurred on board ship and that was traced to the presence of *S. montevideo* in the contents of hens' eggs. Watt also described the isolation of two additional types, *S. cholerae suis* and *S. derby*, from hens' eggs. Later Gibbons (5) succeeded in isolating *Salmonella* types from eggs produced by two naturally infected flocks of hens.

A study of hens artificially infected with *S. bareilly* has been reported by Gibbons and Moore (7). Of 37 eggs laid during the period the organism was

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excreted, they found three with contaminated shells. Gauger and Greaves (4) have reported studies of a similar nature made with turkeys infected with *S. typhimurium.*

This paper deals with bacteriological studies involving two groups of hens, one infected artificially with *S. bareilly* and the other with *S. oranienburg.* Information was sought primarily on three questions: the extent to which hens infected by the oral route may lay contaminated eggs, how long they would continue to excrete the organisms in feces, and where the organisms tended to localize.

Methods

S. bareilly and *S. oranienburg* were the types selected for this study since, except for *S. pullorum*, they were found in egg powder with the greatest frequency by Gibbons and Moore (6). The cultures were obtained from Dr. N. E. Gibbons and represented strains isolated from egg powder. In all cases inoculation into the crop was made orally by the introduction, with a pipette, of 1 ml. of a 24 hr. nutrient broth culture of the organism.

The general plan of the experiments was the same for both organisms, being as follows: (*a*) bacteriological examination of shells and contents of all sound eggs obtained prior to and during the period of artificial infection; (*b*) study of duration of infection using four hens from which daily fecal samples were examined over a period of two to three months; (*c*) localization of organisms was studied using four or five hens that were inoculated and a bird sacrificed and organs examined bacteriologically at four or five day intervals; (*d*) effect of weekly inoculation was studied for a period of three to four months using one hen only.

In all, 19 Barred Rocks were used in these studies, 9 in the *S. bareilly* series and 10 in the *S. oranienburg* inoculated group. Prior to inoculation these hens were kept under observation for a period of three weeks, during which time eggs and fecal samples were examined for the presence of *Salmonella* types; in addition agglutination tests were made with *S. pullorum* antigen and an 'O' antigen of *S. bareilly* or *S. oranienburg.* In all these tests, results were negative, hence it was assumed that the hens were free from *Salmonella* infection of Group C or D types.

The number of birds under test at one time was limited to five. The first group of five hens was kept in individual cages, the floors of which were covered with clean paper each day. A large percentage of the eggs laid by this group was soiled with feces. This was done to obtain information on eggs produced under conditions of filth. The remaining hens were kept in individual cages with wire floors, the feces being collected on trays lined with paper that was changed daily. In the latter instance eggs free from gross fecal contamination were obtained.

Fecal samples were examined within a few hours of being collected with the exception of those obtained on Sundays, which were refrigerated overnight.

The numbers of *Salmonella* organisms present in the feces were estimated by means of the "Most Probable Number" (MPN) technique (7).

The eggs were collected daily and held at room temperature until examined, the holding period ranging from 0 to 20 days. The shells and contents of all eggs were examined for *Salmonella* organisms by methods previously described (2).

A post-mortem examination was made on each hen, including a study of gross appearance, and cultural and serological examinations. Cultural studies consisted of inoculation of two enrichment media, Bacto-Tetrathionate Broth and Brilliant Green Bile 2%, from the following sources: liver, gall bladder, spleen, oviduct, ovaries, two or three of the largest ova, and the contents of the duodenum, upper intestine, lower intestine, and caeca. Following incubation the broth media were streaked on Bacto-SS Agar and colourless colonies checked as described above.

Blood samples were collected when the hens were sacrificed and used in agglutination tests with 'O' antigens of the type with which the bird was inoculated.

Results

S. bareilly Experiments

To determine the duration of experimental infection four hens were inoculated (inoculum contained 990,000,000 per ml.), and fecal samples examined daily for approximately two months. The results of studies made with this group are summarized in Table I. Though three hens seemed unaffected by the inoculation, bird A-1 became morbid on the second day, refusing food and squatting in a corner of the cage, but by the fifth day had apparently recovered. Bacteriological examination of the feces did not uncover any great difference in the *S. bareilly* counts between this hen and the other three, though it carried the organisms for a shorter period. In the hope of discovering the reason for the reaction, A-1 was sacrificed on the 14th day, but no explanation was forthcoming since she appeared normal and was free of *S. bareilly* according to the cultural methods used. The fact that serological tests on this hen were negative seems to argue against the possibility that tissue invasion had occurred. This was the only hen of the entire group of 19 to show signs of illness following inoculation. Of 54 eggs laid by this group of hens during the period *S. bareilly* was being excreted, two were found with contaminated shells.

To gain information on the localization of *S. bareilly* in hens, a second group of four was inoculated (inoculum contained 940,000,000 per ml.), and a bird was sacrificed and a post-mortem examination made at intervals of approximately five days. Table II indicates the results of this experiment. In the case of A-8, it is apparent that the infection did not become established, thus explaining the failure to isolate the organism on post-mortem. *S. bareilly* was isolated from the caeca of A-7 on the fifth day, from the caeca and lower intestine of A-6 on the 10th day, and from the spleen of A-9 on the 16th day. It is suggested that the presence of *S. bareilly* in the spleen of A-9 probably explains the higher titre shown by this hen in the agglutination test.

TABLE I

EXCRETION OF *S. bareilly* BY HENS FOLLOWING ORAL INOCULATION, TOGETHER WITH RESULTS OF EGG AND POST-MORTEM STUDIES

Days since inoculation	Hen							
	A-1		A-2		A-3		A-4	
	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg
1	0	C	0	D	<1	D	0	
2	0		3		0		92	D
3	0		0	D	5		2	
4	<1		>160	D	0	C	0	
5	1		<1		2		0	D
6	0		2	C	<1	C	>160	
7	92		24	C	<1	C	24	D
8	35		0	D	0		160	
9	2		<1		0		<1	D
10	0		0	D	2	C	<1	C
11	0		>160		>160	D	0	C
12	0		>160	C	>160		92	D
13	0		0	C	16,000		170	C
14	0		<1	D	>16,000	C	0	
15			3	D	9200		35	C
16			3	D	1600		1	D
17			0	D	1	C	1	
18			0	C	>16,000		<1	DS
19			5		3	DS	59	C
20			0	D	<1		0	D
21			3		54	D	0	
22			0	C	2		0	
23			0		0		0	
24			0	D	0	D	0	[illegible]
25			0	D	0		0	
26			2	D	>16,000		0	D
27			0	C	92	C	0	
28			0		>160	C	0	D
29			0	D	2		0	
30			0	C	0		0	
31			0		0		0	C
32			0	D	0		0	
33			0	C	>160	C	0	
34			92		0	D	0	
35			0	C	>160		0	D
36			0		0		0	
37			0	D	0		0	
38			0		0		0	
39			0	D	0		0	D
40			0		>160	C	0	D
			1		2		3	
Post-mortem								
Appearance	Normal		Normal		Normal		Normal	
S. bareilly	Not recovered		Not recovered		Not recovered		Not recovered	
Serological tests using 'O' antigen	1000*		3100		2100		3210	

Note: C = *Clean shell.*
D = *Soiled shell.*
S = *S. bareilly isolated from shell.*
1 = *Feces negative to the 55th day, 10 dirty eggs also negative.*
2 = *Feces negative to the 63rd day, three clean and three dirty eggs also negative.*
3 = *Feces negative to the 58th day, four clean and eight dirty eggs also negative.*
* *Serum dilutions of 1 : 20, 1 : 40, 1 : 80, and 1 : 160.*

TABLE II

LOCALIZATION OF ARTIFICIAL *S. bareilly* INFECTION IN HENS AS SHOWN BY POST-MORTEM STUDIES, TOGETHER WITH RESULTS OF FECAL AND EGG EXAMINATIONS

Days since inoculation	Hen							
	A 6		A 7		A-8		A-9	
	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg
1	>160	C	0		>160		>160	
2	>160		24		0		>160	
3	>160		3		54		22	
4	540	C	5		0		1600	
5	9200		17		11		16,000	
6	92,000	C I			0	C	54,000	C
7	5400				0		9200	
8	490				0		490	C
9	32	C			0		5400	C
10	160				0	C	54	C
11					0	C	0	C
12					0	C	0	C
13					0	C	0	C
14					0	C	240	
15					0	C	2	
16					0	C	0	C
					1			
Post-mortem								
Appearance	Perforated duodenum, ruptured ovum		Haemorrhage from right kidney		Normal		Normal	
S. bareilly	Isolated from caeca, lower intestine		Isolated from caeca		Not recovered		Isolated from spleen	
Serological tests using 'O' antigen	1000*		1000		4000		4321	

Note: C = *Clean shell.*
I = *S. bareilly isolated from interior.*
1 = *Feces negative to the 26th day, one clean egg also negative.*
* *Serum dilutions of 1 : 20, 1 : 40, 1 : 80, and 1 : 160.*

It will also be seen from Table II that of 12 eggs laid by the established carriers, A-6 and A-9, *S. bareilly* was isolated from the contents of an egg laid by A-6. Since this egg was clean and was cultured the same day it was laid, there is little reason to suspect that the organism passed through the shell. On the other hand, the post-mortem examination, made four days after the egg was laid, revealed a perforated duodenum and the presence of several agglomerations of fecal material in the peritoneal cavity. This, together with the fact that *Escherichia coli* was found associated with *S. bareilly* in this egg, seems to indicate that the infection probably occurred through the infundibulum. Though the circumstances described above suggest that the perforation had occurred several days previously, there was no indication of peritonitis at the time of autopsy, and culture of the largest clump of fecal material failed to isolate any *Salmonella*. The fact that this hen at no time displayed any sign of illness is considered of interest since it suggests a high level of resistance.

To determine the effect of repeated inoculations, A-5 received one ml. of a 24 hr. broth culture of *S. bareilly* at weekly intervals for 15 consecutive weeks. Results are shown in Table III. It will be seen that the greatest excretion of

TABLE III

EXCRETION OF *S. bareilly* BY A HEN INOCULATED ORALLY AT WEEKLY INTERVALS, TOGETHER WITH RESULTS OF EGG AND POST-MORTEM STUDIES

Hen A-5								
Days since first inoculation	Feces, (MPN per gram)	Egg	Days since first inoculation	Feces, (MPN per gram)	Egg	Days since first inoculation	Feces, (MPN per gram)	Egg
1	0	D	36	0		71	0	D
2	1		37	0		72	>160	C
3	0	D	38	0	C	73	0	
4	2	D	39	0	D	74	>160	D
5	2	C	40	1600		75	8	
6	0	C	41	0	C	76	0	D
7	<1	D	42	54	D	77	0	
8	92	C	43	35	D	78	3	D
9	>160	D	44	<1	D	79	>160	
10	>160	D	45	>160		80	>160	C
11	>160	C	46	0	D	81	0	C
12	24		47	0	C	82	>160	
13	7	D	48	0		83	160	C
14	54	D	49	0	C	84	0	C
15	>16,000	C	50	3	D	85	>160	
16	95		51	>160	D	86	22	
17	5	C	52	54	C	87	5	C
18	16,000		53	0	D	88	0	C
19	>16,000	D	54	0	D	89	3	
20	35		55	0		90	0	C
21	0		56	1	C	91	0	C
22	>160		57	0	C	92	>160	
23	2		58	>160		93	0	C
24	<1		59	>160	C	94	0	C
25	0		60	0	D	95	35	
26	92	D	61	160	DS		1	
27	11,000	C	62	<1				
28	<1		63	0	D			
29	10		64	>160		Post-mortem Appearance	Proventriculus and duodenum enlarged	
30	0		65	>160	D			
31	0		66	0	DI	*S. bareilly*	Not recovered	
32	0		67	0				
33	<1		68	5	D			
34	<1		69	35	D			
35	0		70	1	D	Serological tests using 'O' antigen	4000*	

Note: *C = Clean shell.*
D = Soiled shell.
I = S. bareilly isolated from interior.
S = S. bareilly isolated from shell.
1 = Except for the 99th day, feces negative to the 110th day; 10 clean eggs also negative.
* *Serum dilutions of 1 : 20, 1 : 40, 1 : 80, 1 : 160.*

S. bareilly occurred during the second or third week. In succeeding weeks there was an evident tendency toward high counts the first few days after inoculation, with *S. bareilly* appearing in low numbers or not at all the latter part of the week. Of 60 eggs obtained during the period this hen was a carrier, two yielded *S. bareilly*, in one instance from the shell and in the other from the contents. The only abnormality noticed on post-mortem examination was the enlarged and highly vascularized proventriculus and duodenum. Table III also indicates how well egg production was maintained, except for the fourth and fifth weeks; this, together with the pattern shown by the fecal counts, suggests the development of resistance to repeated oral inoculations.

S. oranienburg Experiments

To determine the duration of artificial infection, four hens were given an oral inoculation of a 24 hr. broth culture of *S. oranienburg*, containing, according to plate count, 770,000,000 organisms. Fecal samples were examined daily for approximately three months and the results are shown in a somewhat condensed form in Table IV. This group was selected from pullets that were just starting to lay, but since they began to moult soon after inoculation, egg production was very low. In all, only 27 eggs were obtained for culture following inoculation; 19 of these were laid by B-1. *S. oranienburg* was not isolated from the shell or meat of any of these eggs.

A finding of interest was the isolation of *S. bonariensis* from the feces of B-1 and B-2 on the 10th and 8th days, respectively, after inoculation with *S. oranienburg*. As far as is known to the author, this is the first evidence of the association of this organism with fowl.

Hen B-3 was sacrificed and examined on the 80th day, after a progressive illness of a week's duration. It was apparently suffering from 'big liver disease'. *S. oranienburg* was not recovered from this hen nor from the remaining three when cultured a few days later.

To study the localization of the organisms, five hens were inoculated with a broth culture that gave a plate count of 860,000,000 per ml. Daily fecal examinations yielded only two *S. oranienburg* cultures, one from B-6 on the second day and one from B-10 on the eighth day, with the MPN per gram being 23 and 5, respectively. A hen was sacrificed at four-day intervals following inoculation, but it was not surprising, in view of the results of the fecal examinations, that no cultures were obtained at autopsy. No explanation can be given for the failure to establish infection in this group, though it was noticed, during the period of observation prior to inoculation, that the intestinal flora of these birds was somewhat different from that of the hens previously studied. Six eggs laid by this group after inoculation gave negative results to cultural studies.

To determine the effect of repeated inoculations, B-5 was inoculated orally with *S. oranienburg* at weekly intervals for 12 consecutive weeks. Fecal studies indicated the same general picture as those of hen A-5 shown in Table III. Four eggs only were obtained and these were negative on cultural

TABLE IV

EXCRETION OF *S. oranienburg* BY HENS FOLLOWING ORAL INOCULATION, TOGETHER WITH RESULTS OF EGG AND POST-MORTEM STUDIES

Days since inoculation	Hen							
	B-1		B-2		B-3		B-4	
	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg	Feces, (MPN per gram)	Egg
1	>160		>160		>160	C	>160	
2	1	C	>160	C	>160		>160	
3	0	C	13	C	220	C	54	
4	92	C	0		0	C	43	
5	0	C	0	C	35		310	C
6	0		0	D	24		4	
7	0		0		0		24	
8	1600		**		0		220	
10	**		0		0		0	
15	0	C	0	C	0		0	
18	0		0		0		>160	
19	0	C	0		0		12	
20	>160	C	0		0		0	
21	0	C	0		0		0	
23	3	C	0		0		0	
24	>160	C	0		0		0	
25	50		22		0		1	
27	0	C	0		0		0	
28	35	C	0		0		0	
29	0		0		0		1	
32	0		0		0		35	
34	0		0		0		1	
35	0		0		0		2	
43	24		0		0		0	
50	81		0		0		0	
57	0		0		1		0	
62	0	C	0		0		0	
63	0	C	0		0		0	
65	0	C	0		0		1	
69	0	C	0		0		0	
71	0	C	0		0		0	
83	0		0		0		3	
84	0		0		0		3	
85	0	C	0		0		0	
87	0	C	0		0		1	
Post-mortem								
Appearance	Normal		Normal		'Big liver'		Ruptured ovum	
S. oranienburg	Not recovered		Not recovered		Not recovered		Not recovered	
Serological tests using 'O' antigen	4210*		3210		0000		1000	

Note: C = Clean shell.
D = Soiled shell.
** Serum dilutions of 1 : 20, 1 : 40, 1 : 80, and 1 : 160.*
*** S. bonariensis isolated.*

examination. Weekly serological tests showed some variation, but the titre at no time was higher than 'one plus' at 1/80 dilution of serum in *S. oranienburg* 'O' antigen. This hen was autopsied at 90 days and was normal in appearance and negative culturally.

Discussion

It is recognized that the small number of hens employed in these experiments places a limitation on the value of the results obtained. For this reason a comparison of the results of the present study of *S. bareilly* infected hens with those of Gibbons and Moore (7), who used six hens, is of especial interest. They reported the excretion of *S. bareilly* from the intestinal tract of orally infected hens over a period of 18 to 38 days, the isolation of *S. bareilly* from the intestinal tract and liver, and also from the shells of 3 of 37 eggs laid while the organism was being excreted. It is evident that the results of the present experiments, namely, a carrier period of 5 to 40 days, the isolation of *S. bareilly* from the intestinal tract and spleen, and from the shells or contents of 5 of 124 eggs laid while the hens were carriers, show favourable agreement. The only significant difference has been the isolation of *S. bareilly* from egg contents. Of interest is the fact that the three eggs found in the present experiment with contaminated shells were classed as 'dirties' while the shells of the two with contaminated contents were clean.

With respect to the results of the *S. oranienburg* experiments, no significance can be attached to the failure to isolate the organism from the eggs because of the small number of eggs examined, and also because the low fecal counts obtained suggest a lower level of infection than that occurring in the *S. bareilly* inoculated hens. In the latter connection it is interesting to note that Edwards and Bruner (3) found the incidence of *S. oranienburg* in fowl to be approximately half that of *S. bareilly*.

Whether the intermittent isolation of *S. oranienburg* from the feces of B-1 and B-4 indicates a prolonged carrier period is open to question since B-5, receiving weekly inoculations, was carried along simultaneously, and could, therefore, conceivably have served as a source of reinfection of these hens or accidental contamination of their feces. Precautions taken against these eventualities were: the housing of B-5 in the bottom row and the other birds in the top row of a three-tier bank of cages; and the use of aseptic technique in handling the feces. As a further precaution against accidental contamination, the sample of feces from B-5 was the last to be taken each day. In addition to these possibilities, sampling error was doubtless large because no attempt was made to mix the total excretion of feces for the 24 hr. period before the samples were taken.

The fact that Gauger and Greaves (4), in their study of artificial and natural *S. typhi-murium* infection in turkeys, isolated the organism from both shell and contents of eggs laid by the former group but from the shell only in the latter instance, emphasizes the importance of securing naturally infected hens for investigations of this nature, if at all possible. Considerable effort has been expended to this end by the author, so far without success.

Acknowledgments

The author wishes to express his thanks to the National Research Council of Canada for its financial assistance; to Dr. N. E. Gibbons, National Research Council, Ottawa, for many valuable suggestions and for supplying cultures and O-sera; and to Miss V. Crossley, Provincial Laboratories, Toronto, for typing cultures.

Grateful acknowledgment is made also to Professor E. H. Garrard, Department of Bacteriology, Ontario Agricultural College, for his continued interest; to the Poultry Department, Ontario Agricultural College, for supplying the hens; and to Miss P. L. Jones and Mrs. P. Burke for their technical assistance.

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

I. A REACTION CHAMBER ADAPTED TO DETERMINE THE EFFECT OF ANTIKNOCKS ON THE RAPID OXIDATION OF FUEL VAPOR AT HIGH TEMPERATURES[1]

By R. O. King[2]

Abstract

Slow combustion experiments by conventional laboratory methods show that metallic dopes such as the iron and nickel carbonyls and tetraethyl lead act as antioxidants in respect of the liquid paraffins present in engine fuel, the effect being especially marked at high temperatures. Such an effect failed to account for the results of certain engine experiments which could be interpreted only on the assumption that the metallic dopes *promoted* oxidation of the 'end gas' which is known to be the seat of knock.

The inconsistencies mentioned justified an investigation of conventional laboratory methods of measuring rate of oxidation. This led to the design of a small scale flow method reaction chamber in which a typical paraffin, such as pentane, containing iron carbonyl in small concentration and mixed with air in combining proportions could be oxidized to final products, without explosion, in a time of exposure of one second or less at temperatures rising to 700° C. Oxidation of the doped pentane was to the final products, carbon dioxide and steam, at all temperatures of reaction, rate of formation of carbon monoxide being barely measurable. On the other hand, the oxidation of pentane alone was accompanied by a profuse liberation of aldehyde, reaching a maximum rate at about 400° C. and giving a negative temperature coefficient of reaction over the range 400° to 500° C. Oxidation of the pentane alone occurred at a much lower rate, over the high temperature range, than when it contained iron carbonyl in the usual small proportion ($\frac{1}{2}$ of 1%).

The new reaction chamber was used less successfully in demonstrating the effect of tetraethyl lead to promote the oxidation of pentane owing to difficulties arising from the properties of lead. A measurable promoting effect was, nevertheless, obtained at all temperatures of reaction.

The text has been restricted to an account of the development of a novel type of reaction chamber and to oxidations of pentane necessary for the purpose. The chamber is of more general application.

Introduction

Conventional laboratory bulb or flow methods yield results for the effect of antiknock substances on the oxidation of hydrocarbons used as engine fuel that are difficult or impossible to reconcile with the behavior of the substances in the combustion space of an engine. The reacting mixture in the usual laboratory apparatus is oxidized slowly and explosion occurs generally in the temperature range 500° to 600° C., unless the tube or bulb is packed. In the engine, however, complete oxidation of the reacting mixture occurs in a small fraction of a second, and the last portion to burn, the 'end gas', is exposed to temperatures rising to 800° C., depending on the compression ratio used. It was considered that the behavior of fuels in the combustion space of an engine might be interpreted in terms of laboratory oxidations if a reaction chamber could be designed to operate without explosion at temperatures above 500° C. and at the same time provide for complete oxidation of fuel vapor in a time comparable with that of an engine combustion period. Experimental work was undertaken accordingly and the degree of success attained is shown by results described in Sections III and IV.

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[1] *Manuscript received May 16, 1947.*
Contribution from Defence Research Board, Ottawa, Canada.

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Section I

REVIEW OF PUBLISHED EXPERIMENTAL RESULTS

The effect of antiknocks such as tetraethyl lead and the iron and nickel carbonyls on the oxidation of hydrogen and the numerous hydrocarbon constituents of engine fuel has been studied by many investigators. Conventional 'flow' or 'bulb' methods of experiment were used and explosion of the combustible mixture undergoing oxidation occurred at temperatures ranging from 500° to 600° C. unless the oxidation space were 'packed'. A complete review of the published experimental results would be lengthy and it will suffice to mention some of the more significant.

Pope, Dykstra, and Edgar (8) using an open tube flow method found that tetraethyl lead tended to inhibit the oxidation of *n*-octane at temperatures rising to 600° C.; inflammation occurred at higher temperatures.

Berl, Heise, and Winnacker (1) using a packed oxidation space were able to observe oxidations at 500° and 700° C. They obtained a more decided antioxidant effect for both tetraethyl lead and iron carbonyl in respect of pentane and hexane and, for example, reported that "by the addition of 1% of iron carbonyl under the conditions stated, the hexane remains practically unchanged; the oxygen remains unused".

Mardles (5) using the bulb method over the temperature range 230° to 320° C. found that tetraethyl lead tended to inhibit the oxidation of hexane at temperatures above 250° C. but promoted the effect at lower temperatures, and in a later publication (6) described experiments, made with a conventional flow method, showing an oxidation promoting effect for either tetraethyl lead or iron carbonyl in respect of hydrogen, methane, and ethane, irrespective of temperature. The inversion of the effect of metallic dopes was mentioned. No explanation was offered other than the quoted opinion of Moureau and Dufraisse that certain substances may act as oxidants in respect of some compounds and as antioxidants in respect of others.

Pidgeon and Egerton (7) using the bulb method at a constant temperature of 265° C. found the oxidation of pentane to be promoted when tetraethyl lead was freshly added; an inhibitory effect was observed after the metal of the dope became oxide.

The experimental work to which reference has been made, as well as a great deal of similar work not mentioned, was initiated in an endeavor to explain the antiknock effect of metallic dopes. Knock was regarded by many as due primarily to an oxidation process beginning with the formation of explosive organic peroxides. The metal of the dope was supposed to destroy the peroxide or, in some way rather difficult to explain, interrupt chain reactions in which peroxides were essential links. The experiments were of the slow combustion type made generally at relatively low temperatures, and it is difficult to use the results as a foundation for a rational explanation of the effect of the dopes on combustion of the end gas in an engine which goes to completion in a small fraction of a second on exposure to temperatures extending to 800° C. The results are, however, in agreement in showing that, *in the conditions in which they were obtained*, the metallic antiknocks inhibit in varying degree the oxidation of the higher paraffins present in large proportion in commonly used engine fuel and mainly responsible for fuel knock. Some doubt was, however, cast on the validity of the antioxidant effect by finding that engine experimental results, not yet described, could be explained only by assuming that the dopes *promoted* oxidation in the related conditions.

The disagreement between laboratory and engine experimental results was discussed with Dr. F. H. Garner, Chief Chemist in England of the Standard Oil Development Co., and Prof. E. K. Rideal. The discussion led to arrangements being made to undertake a series of oxidation experiments, using new methods, in the Colloid Science Laboratory, Cambridge University. The experiments are described in succeeding sections, beginning with a description of the preliminary work required to recover typical oxidation results obtained by others and to devise a reaction chamber to reproduce in some degree the temperature and 'time of exposure' conditions prevailing in the combustion space of a carburetor engine.

Section II

PRELIMINARY EXPERIMENTS AND REACTION CHAMBER NO. 10

Oxidation research is usually conducted with a particular form of a conventional method to determine the characteristics of a number of substances. Thus it seemed that whether metallic antiknocks promoted the oxidation of some substances or inhibited the effect in others or reversed in effect on increasing temperature might depend on the form or scale of the laboratory apparatus. It was decided, therefore, to depart from the usual procedure by selecting one typical liquid paraffin for all the experiments and to confine the variables to the scale and design of reaction spaces.

The flow method of experiment was selected in preference to the bulb method for two principal reasons; (1) it permitted flexibility in the design and scale of the reaction space, and (2) it enabled samples of the reaction products to be withdrawn at any temperature for analysis. The experiments were made with mixtures of pentane vapor with air. The methods of fixing 'mixture strengths', of measuring rate of mixture supply to the reaction space, and of analyzing the oxidation products are described in the appendix.

Typical Oxidation Results (Mardles) for Pentane and Hexane, Conventional Flow and Bulb Methods

The results have already been mentioned, Section I. Those for pentane obtained by Mardles (6) using the flow method are shown graphically by Fig. 1. It will be noted that oxidation begins at about 220° C. and proceeds the more rapidly in the doped mixture until the temperature reaches 400° C. The graphs then cross and at higher temperatures the pentane is oxidized more rapidly than with tetraethyl lead added. The conditions of the experiment are not stated in the text of the reference quoted but it is known that the rate of mixture supply was approximately 1 litre per hour, determined by 'counting bubbles'. The combustion tube was the usual hard glass variety, 12 mm. inside diameter supported horizontally in a tubular electric furnace 12 in. long. The mixture strength was determined by weighing a surface carburetor 'before and after'. Oxidation results obtained by Mardles (5) for

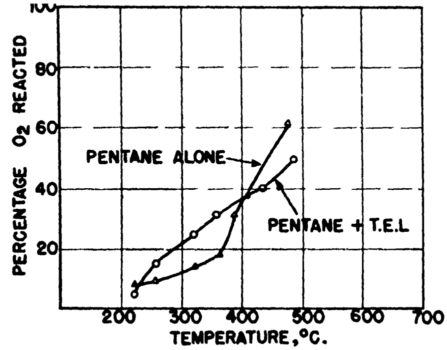


FIG. 1

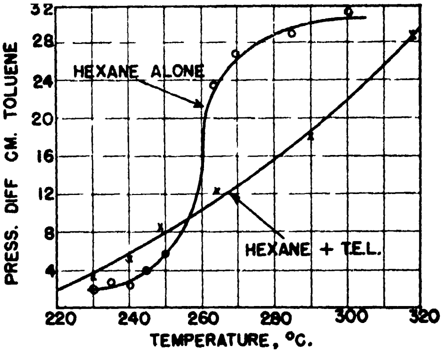


FIG. 2

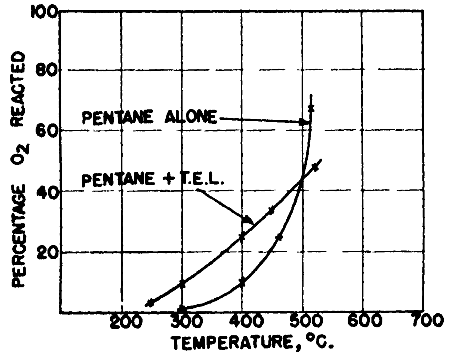


FIG. 3

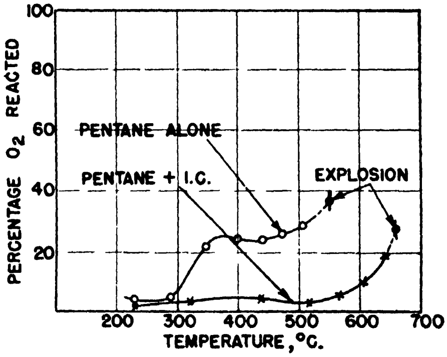


FIG. 4

FIG. 1. *Pentane oxidation (Mardles). Tube method,* $\frac{L}{D} = 25$. *Flow = 16 cc. per min.*

FIG. 2. *Hexane oxidation (Mardles). Bulb method.*

FIG. 3. *Pentane oxidation (King). Tube method,* $\frac{L}{D} = 32$. *Flow = 150 cc. per min.*

FIG. 4. *Pentane oxidation (King). Tube method,* $\frac{L}{D} = 6$. *Flow = 150 cc. per min.*

hexane, using the bulb method, are shown graphically by Fig. 2. Experimental details are given in the reference quoted. It will be noted that the reversal of the oxidation promoting effect of the tetraethyl lead is at approximately 255° C., that is, 145° C. lower than observed for the pentane oxidation.

Effect of Changing Ratio of Length to Diameter of Combustion Tube

The Cambridge experiments were begun with the conventional set up of a combustion tube in a tubular electric furnace except that the furnace was exceptionally long (24 in.), the combustion tube being of Pyrex approximately 19 mm. internal diameter. The L to D ratio was, therefore, 32 instead of 25 as used by Mardles. The results of the oxidation of pentane alone and with the small addition of 0.25% by weight of tetraethyl lead are given by the graphs of Fig. 3. Comparing them with those of Fig. 1, it will be noted that the promoting effect of tetraethyl lead at relatively low temperatures was similar to that observed by Mardles but was maintained until the temperature reached 500° C., that is, 100° C. higher. The experiments showed that the general characteristics of pentane oxidation already described in references given had been recovered. The next significant change in the reaction space was to *reduce* the L to D ratio to 6 by using a furnace 6 in. long and a combustion tube of 1.0 in. internal diameter. A Jena Supramax Glass tube was used in the expectation that it might be possible to carry oxidation to temperatures above 600° C. Temperatures were taken by a ring thermocouple of two junctions surrounding the combustion tube at the position of maximum temperature instead of by the usual arrangement of a couple enclosed in a silica sheath and fixed within the combustion space. The hot upper end of the combustion tube was closed by a stainless steel block provided with an outlet tube and surmounted by a safety cap which blew off in the event of an explosion and prevented damage. All joints were ground and remained tight.

The experimental results for pentane and pentane plus iron carbonyl oxidized in the short wide tube are given by the graphs of Fig. 4. They are quite remarkable in showing a greater *antioxidant* effect than obtained by any others in open combustion tubes—moreover, there was no reversal of the effect; it persisted from the temperature of initiation to that of explosion. Similar results were obtained when the pentane was doped with tetraethyl lead. It will be noted that the explosion temperature increased over 100° C. on adding the antiknock compound to the pentane although rate of reaction *diminished.* It is also noteworthy that with the relatively large diameter tube a 'hump' showing a slight negative temperature coefficient of reaction appears in the graph for the oxidation of pentane undoped. Similar results were obtained when combustion tubes of the same L/D but of different materials were used. The materials tried were nickel-steel, silica, and graphite.

The experiments seemed to have come to a dead end with an exceptionally complete verification of the antioxidant effect of tetraethyl lead in respect of a typical liquid paraffin and consequent confirmation of current theory that the antiknock effect is obtained accordingly. It was evident that if the metallic antiknocks promoted oxidation at high temperatures, as seemed to be indicated by engine experiments, the effect could not be demonstrated by the use of conventional bulb or tube methods, and experiments were begun to design a new type of reaction chamber.

Considerations Leading to the Development of a New Type of Reaction Chamber

It is well known that deposits of metal and various metallic oxides remain on the interior surfaces of combustion tubes after oxidations of doped vapor mixtures. It is difficult to examine the residues in long narrow tubes. Short wide tubes possess the advantage that the deposit can readily be inspected and the nature of that seen at any position related to the corresponding temperature. Moreover, there were in short tubes, when heated, very steep temperature gradients from the middle to the ends, and if the tube were used in a vertical furnace, the deposits were left in fairly distinct successive bands of metal and colored oxides on cooling the furnace and stopping the flow of doped mixture. It was observed for all the short tubes used for the experiments mentioned above that after high temperature oxidations of pentane containing tetraethyl lead or iron carbonyl a metallic mirror, as a band, remained at or near the position of entry of the tube into the furnace. It seemed, therefore, that little if any of the metal yielded by the dope reached the position of maximum tube temperature if that were much above the temperature of decomposition.

Callendar's experiments (2, 3) with organometallic compounds in sealed tubes showed that the decomposition of tetraethyl lead was nearly complete at 215° C. and left a metallic mirror on the surface of the tube. Nickel carbonyl vapor decomposed readily at 150° C., the nickel being deposited on any available surface. Decomposition occurred solely on surfaces, not in the body of the vapor. The characteristic was, in fact, discovered by Mond many years earlier and remains the basis of the commercial method used to procure pure nickel. Callendar's experiments indicate that tetraethyl lead or iron carbonyl vapor when mixed with air and fuel vapor and passed through a heated combustion tube would not reach the seat of a high temperature reaction before being decomposed at a lower temperature to yield metal which would be deposited on contact surfaces and oxidize rapidly in the conditions.

In accordance with the above mentioned considerations, experiments were made to determine the position of iron carbonyl decomposition in a 1 in. diameter Pyrex tube set horizontally in a 6 in. tubular furnace. A pentane–air mixture in combining proportion was passed into the tube at the rate of 150 cc. per min. through a 6 mm. Pyrex inlet tube as shown by Fig. 5. The pentane contained iron carbonyl in the concentration of 0.5%. The reacting mixture was allowed to flow for two hours while the temperature indicated by a ring thermocouple surrounding the tube at the middle of the furnace was maintained at 400° C. The tube was used in the horizontal position because the deposits of metal and oxides give a better indication of the path of the mixture than when the tube is vertical and the deposits appear as bands.

The traces remaining on the tube on completion of the experiment were photographed and are shown in elevation and plan by *A* and *B*, Fig. 5. They indicate the path of the mixture in the tube to be as shown by *C* of the same figure. The entering mixture, being relatively cool, falls in a stream and leaves a small iron mirror where it strikes the bottom surface. It is then heated by contact with the glass and rises through the relatively cool mixture in the entrance end of the tube, the rising stream being divided by the small mixture admission tube on which deposits of red oxide are left. The stream then strikes the top of the tube receiving more heat and moves toward the middle. The markings show, however, that it falls away from the top surface, presumably when it reaches mixture of higher temperature and consequently lower density.

It appears that when gaseous mixtures at room temperatures are admitted to the cool end of a combustion tube a heating eddy is formed. Similarly a cooling eddy is formed when the mixture leaves through a central outlet.

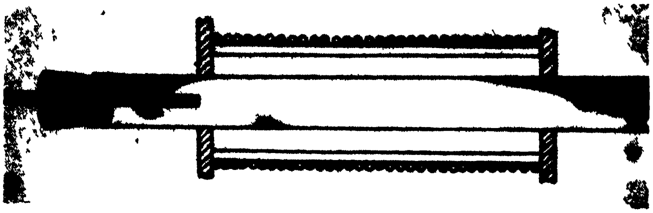
Except for the small iron mirror already mentioned, all the deposits from the eddy in the entrance end were red oxide and apparently nothing but that substance passed through the middle part, which is the position of maximum temperature and generally assumed to be that of the greatest degree of oxidation activity. That it did pass through was shown by the heavy deposit of oxide from the exit eddy.

The experiment was of general interest in showing that 'exposure time' as usually calculated is in error, but the point of immediate interest was the demonstration that the metal of the dope in a gaseous mixture passed through a conventional type of combustion tube tends to be deposited on surfaces at or near the entrance of the heating furnace as the temperature is raised. The deposition would be expected to increase with the magnitude of the entrance eddy, which in turn increases with increase in the tube diameter or a decrease in *L* to *D* ratio. Thus an explanation is afforded for the experimental results of Figs. 1, 3, and 4, showing that the antioxidant effect of the dope increases as the *L* to *D* ratio of the combustion tube diminishes. Obviously the effect of metallic dope on oxidation, as observed in engine experiments, would be reproduced in laboratory experiments only if the dope were introduced into the actual reaction space before being decomposed. The experiment showed very definitely that this condition cannot be met with the conventional straight-through combustion tube arrangement.

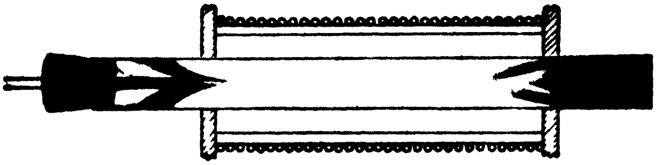
Reaction Chamber No. 10

The problem of designing a reaction chamber suitable for ensuring that the metal yielded on the decomposition of the dope content of pentane is present at the position of a high temperature reaction in a pentane–air mixture was not easy of solution. Reasonable finality of design was achieved with Reaction Chamber No. 10, illustrated by Fig. 6, *A* and *B*. *A* shows the complete arrangement as set up in an electric furnace and *B* an enlarged section of the reaction chamber and adjacent parts.

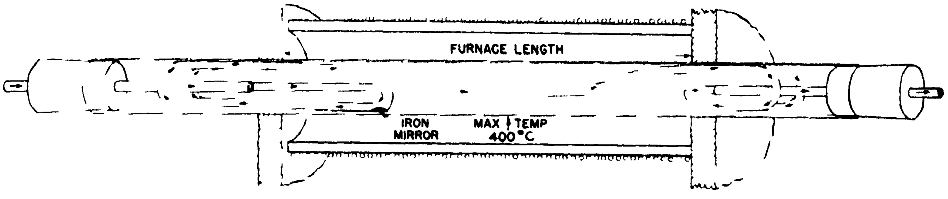
PLATE I



A Side view of combustion tube



B. Plan view of combustion tube



C Indicated path of a filament of the mixture

FIG 5 *Showing the effect of heat convection on the flow path of a doped pentane–air mixture through a conventional combustion tube and the very small area on which metal is deposited as a mirror*

It will be seen by reference to the figure that the reaction chamber is an inverted cup formed in the end of a tube which is contained within another of sufficiently large diameter to provide an annulus about 1.0 mm. wide for the escape of gas from the reaction space. The tubes may be of any material suitable for use at high temperatures, provided the decomposition and oxidation products of metallic dope will adhere to the heated surfaces. The lower end of the cup is nearly closed by an asbestos cement washer, fitting closely in the outer tube and having a small central hole through which the gaseous reacting mixture is admitted as a jet from a small orifice in the top of a water cooled inlet device. It is important that the opening from the reaction chamber into the annulus should be no greater than required to avoid appreciable resistance to the gas flow. The orifice was usually 1.0 mm. diameter but must be of such a size that the jet created by the mixture passing through it will maintain a streamline form until it strikes the top of the reaction chamber; preliminary experiment showed that in the circumstances metallic dope in the reacting mixture does not decompose until contact is made with the surface. The arrows, Fig. 6, *B*, show the path of the reacting mixture from the admission orifice, through the reaction chamber to the annulus and thence upward to the outlet tube at the upper end of the apparatus.

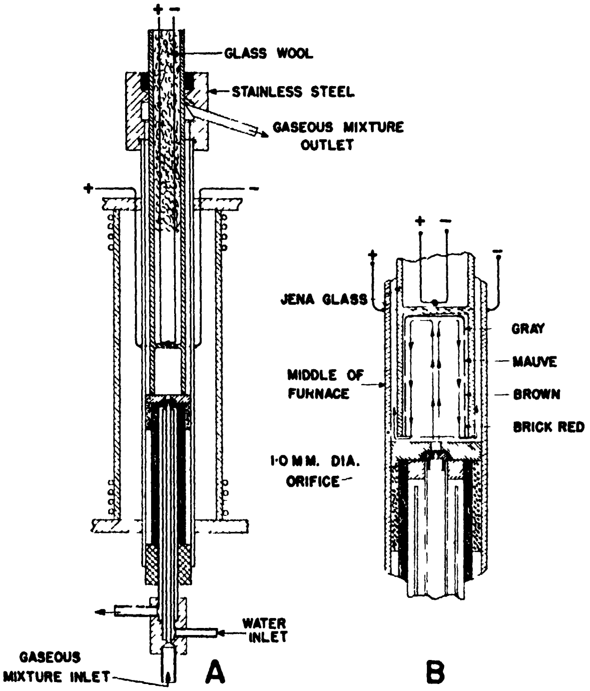


FIG. 6. *General arrangement of Reaction Chamber No. 10 in electric furnace and enlarged section of chamber.*

The reaction chamber as used for most of the experiments was 12 mm. diameter and 22 mm. long, the volume being 2.5 cc. The reacting mixture was generally supplied at the rate of 150 cc. per minute, that is, sufficient to fill the chamber 60 times per minute. The reaction space of a four stroke internal combustion engine is filled at the same rate when the speed is 120 r.p.m.

The reaction chamber was supported in an electric furnace and thermocouples for temperature measurement arranged as shown by the diagrams, Fig. 6. A pair of thermocouples made up of a wire ring, half iron and half constantan, giving junctions at opposite ends of a diameter, was used to measure 'outside' or furnace temperature. The ring fitted easily over the outer glass tube and the connections leading to an indicator are shown by the figure. A single thermocouple was used to measure the 'inside' temperature on the top of the reaction chamber. The thermocouples and the related indicators were supplied by the Cambridge Instrument Company.

Jena Supramax glass reaction chambers were used for determining the effect of iron carbonyl on the oxidation of pentane. This variety of glass remains hard at temperatures exceeding 700° C. and resists attack by metallic oxides at lower temperatures. Decomposition and oxidation products of the carbonyl do not adhere to the glass until after a doped pentane–air mixture has been passed through the chamber for a short time while the temperature is maintained at about 700° C. The preliminary treatment effects a slight roughening of the glass. The chamber cannot properly be used for pentane oxidations after use with mixtures containing dope unless it is cleaned with hydrofluoric acid and washed with steam.

The device for ensuring that unheated doped pentane–air mixture entered the reaction chamber is shown at *A* and *B*, Fig. 6. The device was, of course, a cold body with the upper part adjacent to the high temperature reaction chamber and it was necessary to insulate it as thoroughly as possible. The insulation comprised the asbestos cement washer already mentioned and, in addition, the body of the device was wrapped with layers of asbestos paper and the upper part wound with asbestos yarn to form a plug fitting tightly in the outer tube. The insulation arrangements are illustrated by *B*, Fig. 6. The water cooled inlet device may have caused some cooling of the lower end of the reaction chamber, but at least partial compensation was obtained by adjusting the apparatus in the furnace to bring the top of the reaction chamber slightly above the position of maximum temperature. The diagram *A*, Fig. 6, is in error in showing the chamber below the position of maximum temperature. In any event, reacting mixtures, passed through the chamber at much higher rates than generally used for laboratory experiments, could be raised to the temperatures, about 700° C., required for complete oxidation.

The upper ends of the tubes of the reaction chamber became extremely hot when oxidation temperatures ran to 700° C. Rubber connections could not be used, and a special device illustrated by *A*, Fig. 6, was found to be satisfactory. The upper end of the outer glass tube was ground flat and made a joint on a flat surface of the stainless steel block. The inner glass tube passed through the block, in which a recess in the nature of a 'stuffing box' was turned. The recess was packed with asbestos.

Section III

Trials of Reaction Chamber No. 10

A combining proportions mixture of air with pentane containing iron carbonyl in the concentration of 0.5% by volume was supplied to the chamber at the rate of 150 cc. per min. and samples of oxidation products taken for analysis while the temperature was raised by steps to 700° C. The upper graph of Fig. 7 shows the rate of oxygen reacted plotted against temperature.

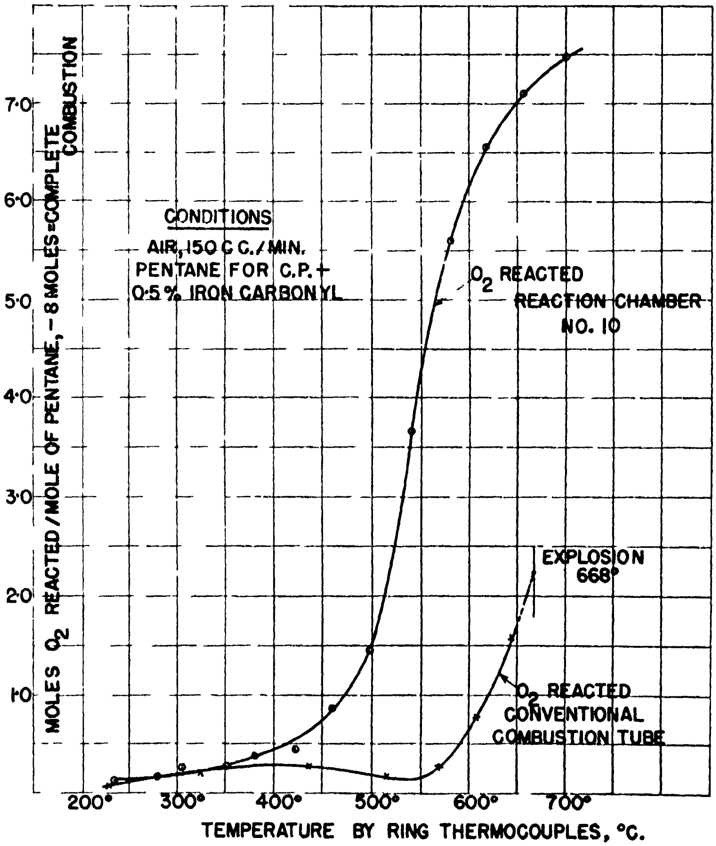


Fig. 7. *Rate of oxidation of a doped pentane-air mixture in Reaction Chamber No. 10 compared with the rate in a conventional combustion tube.*

The lower graph of the figure shows the rate at which oxygen was reacted when a similar mixture was passed through a conventional open combustion tube, 25.0 mm. diameter in a 6 in. furnace, at the rate of 150 cc. per min., as described in Section II with reference to Fig. 4.

The design of the reaction space constituted the sole difference between the conditions of the two experiments but the oxidation results differed in a somewhat remarkable manner, thus, (*a*) oxidation in Reaction Chamber No. 10 occurred at an extremely high rate especially at temperatures above 500°

At 600° C. the rate was 6.2 moles of oxygen reacted as compared with 0.7 moles in the conventional combustion space having a volume 30 times greater if the length of tube inside the furnace is as usual regarded as reaction space, (*b*) the doped mixture did not explode in Reaction Chamber No. 10 in spite of the high rate of reaction, reaching substantial completion at 700° C. On the other hand a similar mixture in the combustion tube exploded at about 668° C. and the last sample taken before the event showed that only 1.6 moles of oxygen had reacted. Rates of oxygen reacted, and of carbon oxides formed, in Reaction Chamber No. 10 are shown by the graphs of Fig. 8. It will be noted that carbon monoxide formation was inappreciable, indicating that oxidation was to the final products, carbon dioxide and steam, at all temperatures of reaction.

The colors of the deposits on the surface of the Reaction Chamber were as shown at *B*, Fig. 6. They appeared in distinct bands beginning with gray (iron) which covered the top of the chamber and extended a short distance down the wall, then mauve, brown, and finally brick red. The colors show the progress of oxidation of the iron in the carbonyl as it passes from the top to the bottom of the reaction chamber.

Oxidation of Pentane (Undoped) in Reaction Chamber No. 10

The pentane–air mixture in combining proportions failed to explode when passed through the chamber although the temperature was raised to 660° C. The mixture was supplied as before at the rate of 150 cc. per min. The rates of oxygen reacted are given by Graph *A* of Fig. 9. Graph *B* for doped pentane, reproduced from Fig. 7, is shown for comparison.

It will be seen by reference to the graphs that the pentane alone is oxidized at a greater rate than when doped, over the temperature range 330° to 500° C. This is the temperature range of aldehyde formation and the graph shows what became known in subsequent work as the 'aldehyde hump' with a marked ***negative*** temperature coefficient of reaction. The rates of formation of carbon oxides are shown by the graphs of Fig. 10 and are significant of aldehyde formation. It is of interest to compare them with the graphs of Fig. 8, which show an almost complete absence of carbon monoxide in the oxidation products of the doped pentane.

The temperature region above 500° C. is of special interest because one of the objects of the investigation was to provide means for working in the temperature range of the 'end gas' in an engine. The very great effect of the carbonyl to promote oxidation at high temperatures will be noted. Thus, referring to Fig. 9, at 600° C. with 0.5% of iron carbonyl in the pentane, 6.2 moles of oxygen were reacted to form carbon dioxide and steam whereas without the carbonyl only 1.4 moles of oxygen were reacted and oxidation was not to final products.

Inside and Outside Temperatures

The ring thermocouples surrounding the outer tube of the reaction chamber would be expected to indicate a higher temperature than the couple resting on the top of the reaction chamber and indicating more nearly the temperature of the chamber. Outside temperatures were, however, used for plotting results, merely to continue the practice begun before the development of a separate reaction chamber within an outer tube.

When pentane alone was oxidized in the chamber, outside temperature was the higher by 17° C. at the beginning of the experiment. The difference reached a maximum of 25° C. at reaction temperatures of about 500° C. and then diminished to again become 17° C. at 600° C. The initial difference was again about 17° C. in the experiment with doped pentane, as would be expected. A maximum difference of 20° C. occurred at 400° C. and thereafter diminished to become 13° C. only at 700° C.

The inside thermocouple rested on the top surface of the reaction chamber and the temperature differences given are consistent with the view that reaction occurred mainly on the upper surface of the chamber. The temperature differences show that the rate of heat liberation was the greater when doped pentane was oxidized, as would be expected.

Section IV

OXIDATION OF PENTANE DOPED WITH TETRAETHYL LEAD IN REACTION CHAMBER NO. 10

It is evident from the experiments described in Sections II and III that the rapid oxidation in Reaction Chamber No. 10, of pentane doped with iron carbonyl, was a surface effect probably occurring mainly on iron deposited on decomposition of the carbonyl. The iron so obtained covered a considerable part of the reaction chamber surface as shown at *B*, Fig. 6, and mentioned earlier. An equal area of metal would not be expected when using lead dope because the surface of the chamber must be heated to a temperature far above the melting point of lead (327° C.) if the pentane is to be oxidized at an appreciable rate. Moreover, lead oxidizes with great rapidity in the conditions and the oxides tend to dissolve in glass at high temperatures. Thus after passing a pentane–air mixture doped with tetraethyl lead through the glass reaction chamber at high temperatures the wall surface remained smooth but discolored. There was, however, on the top surface a slight metal coating in the form of a disk about 4.0 mm. diameter covering the spot where the jet of cool reacting mixture impinged. The disk was surrounded by a ring of orange colored oxide about 1.0 mm. wide. Beyond it was a wider ring of light yellow grading off to chalk white. Similar deposits were procured in some quantity from other experiments and the chalk white substance identified as a lead oxycarbonate, $PbO.2PbCO_3$. The yellow color indicated that some PbO remained in the oxycarbonate.

In spite of the difficulties it was possible by using a steel reaction chamber to obtain conditions in which tetraethyl lead acted to promote the oxidation of pentane at temperatures ranging to 650° C., although the effect was much smaller than observed for iron carbonyl, as would be expected in view of the

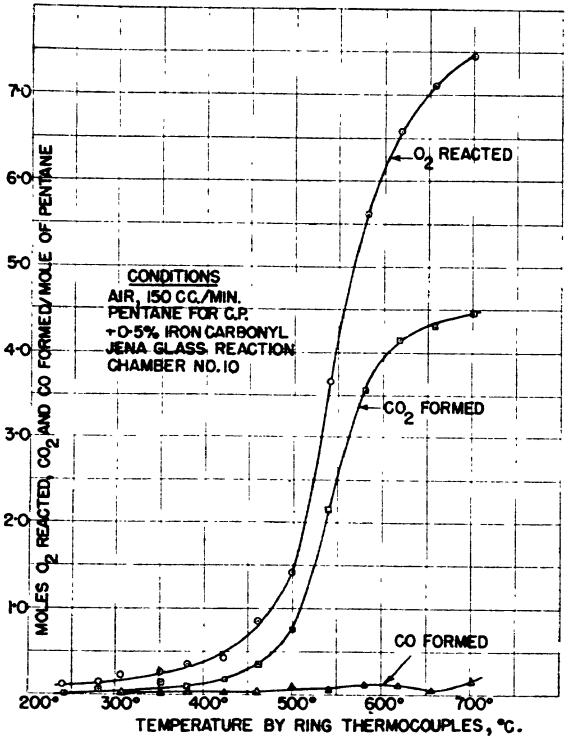


FIG. 8

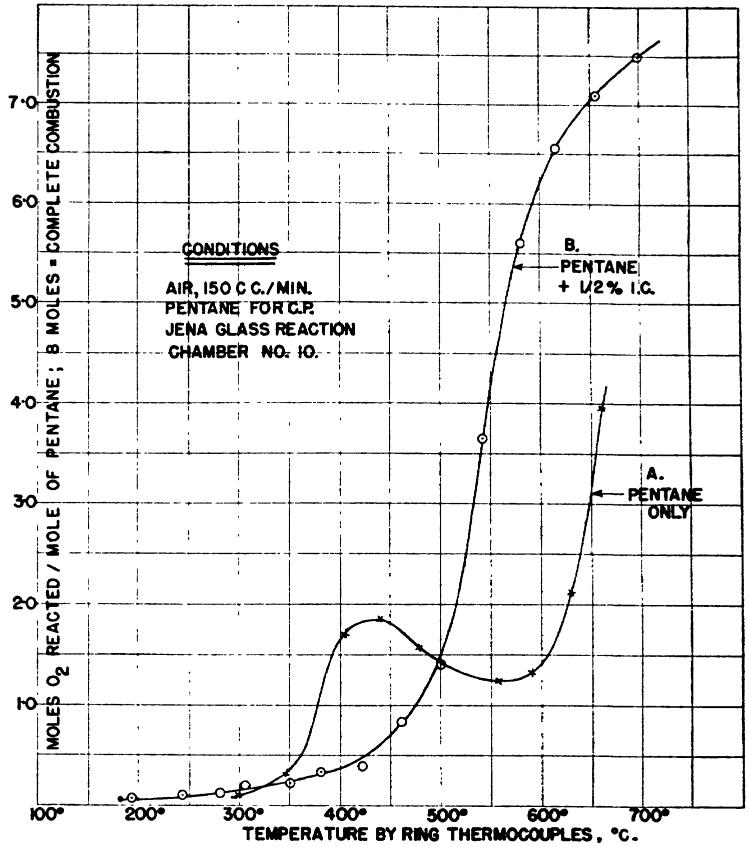


FIG. 9

FIG. 8. *Rates of carbon monoxide and carbon dioxide formation when doped pentane is oxidized in Reaction Chamber No. 10.*

FIG. 9. *The effect of iron carbonyl on the oxidation of pentane in Reaction Chamber No. 10.*

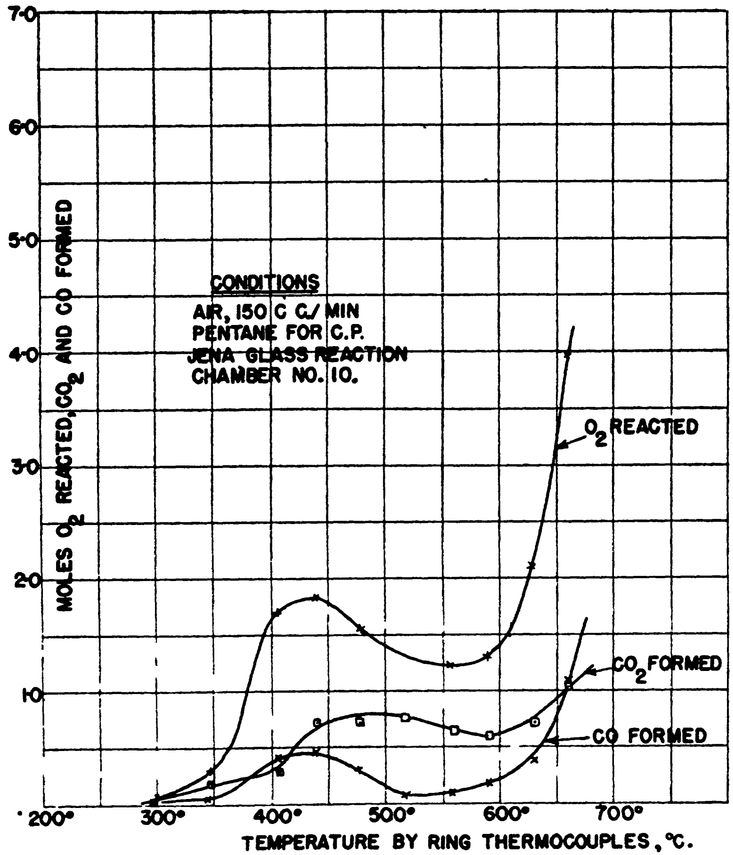


FIG. 10

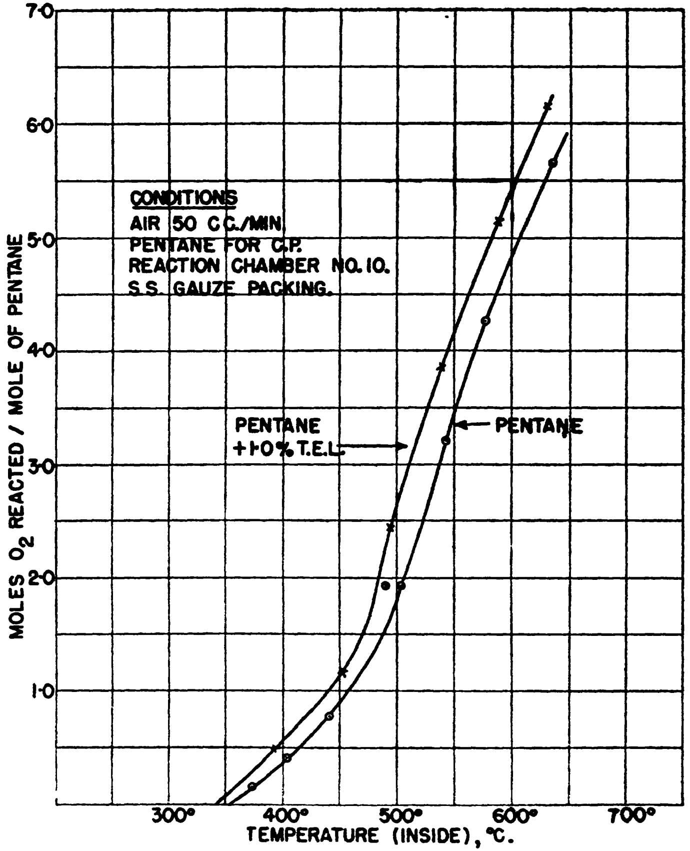


FIG. 11

FIG. 10. *Rates of carbon monoxide and carbon dioxide formation when pentane (undoped) is oxidized in Reaction Chamber No. 10.*
FIG. 11. *Effect of tetraethyl lead on the oxidation of pentane in Reaction Chamber No. 10 (packed)*

circumstances mentioned. The design was similar to that of the Jena glass chamber illustrated by Fig. 5, but a roll of stainless steel gauze was placed in the reaction space to increase the area of surface on which deposition of metal from the dope might occur. The jet of entering mixture passed into and through a central hole in the roll of gauze.

The results of oxidations of pentane alone and pentane containing tetraethyl lead in the concentration of 1.0% are given by the graphs of Fig. 11. Temperatures are as given by an 'inside' thermocouple because the 'ring' thermocouples could not be used in contact with a steel tube. Referring to the graphs it will be noted that the 'aldehyde hump' with a negative temperature coefficient of reaction has disappeared and that rate of reaction is the higher for the doped pentane at all temperatures to 650° C. with 75% of the oxygen reacted. At the temperature of 500° C. rate of oxygen reacted increased from 1.8 to 2.6 moles (44%) on the addition of the dope—the difference remained fairly constant as the temperature increased to 650° C. The oxidation promoting effect of the tetraethyl lead over the high temperature range is of special interest because it is the opposite to that obtained in conventional combustion tubes. The reacting mixture was supplied to the reaction chamber at the rate of 50 cc. per min., so moles of oxygen reacted represent a lower rate of reaction than when the rate of supply was 150 cc. per min. as for the iron carbonyl experiments. The lower rate of reaction and the lack of an aldehyde hump are attributed to the effect of packing the reaction chamber.

Section V

REVIEW OF THE EXPERIMENTAL RESULTS

Although the temperature and time of exposure conditions in an engine combustion space are approached in Reaction Chamber No. 10, an important other condition is not obtained. Thus the end gas in the engine is raised to an extremely high temperature* by compression while contained by relatively cool walls, except for the exhaust valve surface, but the mixture passing through Reaction Chamber No. 10 is raised in temperature by contact with the heated walls.

The metal deposited on the relatively cool walls of the engine cylinder could persist as such for a longer time in an oxidizing atmosphere than when deposited on the hot walls of Reaction Chamber No. 10. This feature is illustrated by the difficulty of maintaining lead as compared with iron on the surface of the reaction chamber. The catalytic activity of any metal coating would, however, be expected to increase with rise in temperature. Thus the upper graph of Fig. 7, for the oxidation of pentane doped with iron carbonyl, shows a gradually increasing rate of oxidation as the temperature rises from 200° C., but over the range 500° to 580° C. the rate increased from 1.5 to 5.6 moles, that is, about 400% for a rise of 80° C. The rate of change of reaction was in fact so great, as indicated by the slope of the graph, that a reliable observation at 540° C. was obtained only after very careful stabilization of temperature and other conditions. The rate of change of oxidation diminishes over the temperature range above 580° C. merely because reaction tends tocompletion.

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* *It is calculated from reliable indicator diagrams that when combustion is 90% complete in an engine, the temperature of the remaining unburnt mixture (end gas) has been raised by compression to 670° C. when the compression ratio is 4 to 1, and to 800° C. when it is 8 to 1.*

The experiments with Reaction Chamber No. 10 indicate that the oxidation of doped pentane is a heterogeneous reaction. If, contrary to accepted theory, the oxidation of pentane occurs similarly, aldehyde formation depending merely on the nature of the contact surface, a simple fundamental explanation would become available for all the phenomena associated with the effect of metallic dopes on combustion in the engine. It is hoped that experiments made accordingly can be described in a subsequent publication.

Acknowledgments

The experimental work described in this paper is part only of that carried out in the Colloid Science Laboratory, Cambridge, with the co-operation of Prof. E. K. Rideal and Dr. F. H. Garner.

The laborious and accurate gas analyses work was undertaken by Mr. R. R. Davidson, Emmanuel College, Cambridge, to whom credit is given for improvements in methods of using the Ambler apparatus.

Dr. E. W. R. Steacie and Dr. L. Marion, both of the National Research Council, have assisted by reading text and advising accordingly.

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APPENDIX

Methods of Measurement

Extended experimental work on oxidation, using a flow method, requires analyses of hundreds of gas samples and convenient methods of supplying reacting mixtures of known composition at known rates. The methods used for the experiments of Sections II to IV will be described briefly in order to indicate that measurements were made with sufficient accuracy; a detailed description is unnecessary for present purposes and would require separate publication.

Gas Analysis

When pentane–air mixtures flowing through a conventional combustion tube are raised to high temperatures, such oxidation as may be obtained is accompanied by the liberation of clouds of smoke, indicating that the gas issuing from the reaction space would contain some products of decomposition such as methane, hydrogen, and unsaturateds as well as those desired, namely, products of oxidation. A complete analysis would, therefore, be tedious and difficult. When, however, similar mixtures were passed through Reaction Chamber No. 10, oxidation generally occurred with great velocity at high temperatures and the course of the reaction could then be followed by determinations of oxygen reacted, and of carbon monoxide and carbon dioxide formed, using an Ambler gas analysis apparatus.

Gas Samples:—The gases from the reaction chamber were passed through at least two condensers, the first cooled by water–ice and the second by solid carbon dioxide in acetone. The uncondensed gas could then, in the absence of appreciable pyrolysis, be assumed to contain only nitrogen, oxygen, and carbon oxides. Samples enough for two analyses were taken in 15 cc. test tubes by mercury displacement and the tubes transferred while still in the mercury trough to individual 10 cc. crucibles and stored in racks.

'Pentane' and Combining Proportions Mixtures:—The pentane, supplied by the Anglo-American Oil Company, was procured by fractional distillation from aromatic free petroleum spirit; distillation range 30° to 40° C., 60% being recovered below 33.5° C. The molecular composition was taken to be C_5H_{12} and, assuming that air contains 20.9% of oxygen, the combining proportions mixture as admitted to the reaction chamber contains the gases in the proportion of 1 mole of pentane to 8 moles of oxygen to 30.3 moles of nitrogen. The accuracy of analysis depends on the proportion of nitrogen in the reacting mixture being known and if the reacting mixture contains oxygen and pentane in correct combining proportions, then when oxidation is *complete*, nitrogen and carbon dioxide only should be found in the gas collected from the condenser, a result which was sometimes achieved.

Air Supply:—The air supply was obtained from the usual high pressure storage cylinders and was, therefore, nearly dry. The air discharged through two-stage regulators (British Oxygen Co.) and any desired rate of flow could be kept nearly constant. The air passed from the regulator through long glass capillary tubing and rate of flow was determined by pressure difference, the capillaries being calibrated *in situ* by the displacement method.

Pentane Supply:—Pentane was required at a small constant rate. The rate is 0.470 gm. per hr. for a combining proportions mixture with air at 20° C. supplied at the rate of 100 cc. per min. The pentane was supplied at any desired rate by a Rideal microdoser (4).

Carburetor:—The very simplest form only is required, especially with the more volatile fuels. The carburetor used for the experiments is illustrated, reference (4), and to ensure thorough mixing of the air and pentane vapor a length of about 3 ft. of ½ in. diameter glass tubing was interposed between the carburetor and the reaction chamber.

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